

Designation: D3606 – 20^{ε1}

Standard Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography¹

This standard is issued under the fixed designation D3606; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—Editorially updated research report information in August 2020.

1. Scope*

1.1 This test method covers the determination of benzene and toluene in finished motor and aviation spark ignition fuels by gas chromatography. This test method has two procedures: Procedure A uses capillary column gas chromatography and Procedure B uses packed column gas chromatography. Procedures A and B have separate precisions.

1.2 The method working range for benzene is in the expected concentrations of: (1) Procedure A between 0.12 % and 5.2 % by volume and (2) Procedure B between 0.10 % and 5.0 % by volume.

1.3 The method working range for toluene is in the expected concentrations of: (1) Procedure A between 0.4 % and 19.7 % by volume, and (2) Procedure B between 2.0 % and 20.0 % by volume.

1.4 For benzene by Procedure A, the following oxygenated fuels are included in the working range: (1) ethanol up to 20 % by volume (E20); (2) methanol up to 10 % by volume (M10). Fuels M85 and E85 were excluded.

1.5 For benzene by Procedure B the following oxygenated fuels are included in the working range: (1) ethanol up to 20 % by volume (E20); (2) methanol up to 10 % by volume (M10). Fuels M85 and E85 were excluded.

1.6 For toluene by Procedure A the following oxygenated fuels were included in the working range: (1) ethanol up to 20 % by volume (E20); (2) M85 and E85.

1.7 For toluene by Procedure B the following oxygenated fuels are included in the working range: (1) ethanol up to 20 % by volume (E20); (2) M85 and E85.

1.8 Procedure A uses MIBK as the internal standard. Procedure B uses *sec*-butanol as the internal standard. The use of Procedure B for fuels containing blended butanols requires that

sec-butanol be below the detection limit in the fuels as *sec*-butanol is an internal standard. For Procedure B, an alternative separation column set described in the annex (A2.3, Annex Approach B) uses MEK as the internal standard when butanols may be blended into gasolines.

1.9 This test method includes a relative bias section for benzene reporting based on Practice D6708 bias assessment between Test Method D3606 Procedure B and Test Method D5769. It is intended to allow Test Method D3606 Procedure B to be used as a possible alternative to Test Method D5769. The Practice D6708 derived benzene correlation equation is applicable for benzene measurements in the range from 0.04 % to 2.53 % by volume as reported by Test Method D3606 Procedure B. The correlation complies with EPA's Performance Based Measurement System (PBMS).

1.10 Correlation equations are included in the relative bias section 13.2.1 of Procedure A to convert Procedure A to the Procedure B volume percent values for benzene and toluene. The correlations are applicable in the concentration ranges of 0.07 % to 5.96 % by volume for benzene and 0.36 % to 20.64 % by volume for toluene as reported by Procedure A. The bias corrected Procedure A to Procedure B result may be correlated further to benzene obtained by D5769 as described in 13.2.1.4(2) of Procedure A and 26.2.1 of Procedure B.

1.11 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.12 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.13 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

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*A Summary of Changes section appears at the end of this standard

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2. Referenced Documents

2.1 ASTM Standards:²

- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D5769 Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants
- D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
- E288 Specification for Laboratory Glass Volumetric Flasks
- E694 Specification for Laboratory Glass Volumetric Apparatus
- E969 Specification for Glass Volumetric (Transfer) Pipets
- E1044 Specification for Glass Serological Pipets (General Purpose and Kahn)
- E1293 Specification for Glass Measuring Pipets

PROCEDURE A—CAPILLARY WCOT GAS CHROMATOGRAPHIC SYSTEMS

3. Summary of Test Method

3.1 An internal standard, methyl isobutyl ketone (MIBK) is added to the sample which is then introduced into a heated capillary or programmed temperature vaporization (PTV) injector on a gas chromatograph (GC). The GC is equipped with two columns connected in series. The sample passes first through a column with a nonpolar phase. After toluene has eluted, the flow through the nonpolar column is reversed, flushing out the components heavier than toluene. The toluene and lighter components enter a second column which separates the aromatic and nonaromatic compounds. The eluted components are detected by a flame ionization detector (FID). The detector response is recorded, the peak areas are measured, and the concentration of each component is calculated with reference to the internal standard.

4. Significance and Use

4.1 Knowledge of the concentration of benzene may be required for regulatory use, control of gasoline blending, and/or process optimizations.

5. Apparatus and Chemicals

5.1 *Chromatograph*—Any gas chromatograph that has the capability of performing multidimensional chromatography that can be operated at approximately the conditions described

in this method, and meets all the required chromatographic specifications and method criteria specified in 7.5 and 11.

5.1.1 *Sample Introduction System*—Automated sample injection system such as a liquid autosampler.

5.1.2 *Injector*—Capillary split/splitless injector.

5.1.3 *Detector*—At least one flame ionization detector (FID) is required. In a two FID configuration, the optional second detector is used to monitor the effluent from the pre-column (refer to configuration A in 7.1.1).

5.2 Columns:

5.2.1 *Pre-column*—Non-polar, boiling point column, which performs the first separation of the hydrocarbons. A dimethyl polysiloxane phase column with dimensions of 30 m by 0.25 mm by 0.50 μ m has been used successfully. Any column with equivalent or better chromatographic efficiency and selectivity may be used.

5.2.2 *Analytical Column*—This column separates aromatic and non-aromatic compounds. A polyethylene glycol (polar 'wax') column with the dimensions 60 m by 0.32 mm by 1.0 μ m has been used successfully. Any column capable of meeting the resolution requirement in 7.5 may be employed.

5.2.3 *Restrictor*—Uncoated deactivated fused silica. A 100 μ m by 42.5 cm restrictor was successfully used when developing this method.

5.3 *Chromatography Data System (CDS)*—An electronic device capable of graphical presentation and integration of the chromatogram peaks.

5.4 *Microsyringe*—Capable of making injections from 0.5 μ L to 1.0 μ L.

5.5 *Volumetric Pipets, Class A*—0.5 mL, 1 mL, 5 mL, 10 mL, 15 mL, and 20 mL capacities (see Specifications E694 and E969).

5.6 *Measuring Pipets*—1 mL and 2 mL capacities calibrated in 0.01 mL; 5 mL calibrated in 0.1 mL, for use in dispensing volumes of benzene and toluene not covered by the volumetric pipets (see Specifications E1044 and E1293) during preparation of standard samples (see 8.1).

NOTE 1—Other manual or automated volume dispensing equipment capable of delivering the specified volumes within the stated tolerance limits may be used as an alternative to the requirements stated in 5.5 and 5.6.

5.7 *Flasks*—Volumetric, 25 mL and 100 mL capacity (see Specification E288).

5.8 *GC Carrier Gas*—Helium or hydrogen 99.999 % pure. (**Warning**—Compressed gas under high pressure; hydrogen flammable.) A hydrogen generator may be used.

NOTE 2—When using hydrogen carrier gas, use precautions such as installation of hydrogen sensors in the gas chromatograph oven. It is recommended that the hydrogen excess flow, such as from the splitter inlet, should be vented to a safe area such as a ventilated hood or appropriate exhaust approved for such use. Use caution when performing maintenance by isolating the hydrogen source.

5.9 *FID Gas*—Air chromatographic grade, dry (**Warning**—Compressed gas under high pressure.) An air generator may be used with purifier.

5.10 *FID Gas*—Hydrogen, 99.999 % pure (**Warning**—Compressed gas under high pressure; hydrogen flammable.) A hydrogen generator may be used.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

5.11 *FID Make-up Gas, if Required (Refer to Manufacturer's Requirements)*—Nitrogen, 99.999 % pure. (**Warning**—Compressed gas under high pressure.)

NOTE 3—Reference the instrument manual for specifics on how to establish required flow rates for a particular vendor's instrument.

5.12 *Chemicals*—(**Warning**—These chemicals are dangerous, harmful, or fatal if swallowed or inhaled. They are flammable to extremely flammable. Vapors can cause flash fires.)

5.12.1 *Internal Standard*—Methyl Isobutyl Ketone (MIBK) 99.5 % pure.

5.13 *Calibration Standards:*

5.13.1 *Benzene*—99.5 % minimum purity. (**Warning**—Carcinogen.)

5.13.2 *Toluene*—99.5 % minimum purity.

5.13.3 *Isooctane (2,2,4-trimethyl pentane)*—99.5 % minimum purity. This is the solvent used for dilution.

5.14 *Method Chemicals for Resolution Validation:*

5.14.1 *Sec-butanol*—99.5 % minimum purity.

5.14.2 *Iso-butanol*—99.5 % minimum purity.

5.14.3 *n-butanol*—99.5 % minimum purity.

5.14.4 *n-propanol*—99.5 % minimum purity.

5.14.5 *Ethanol*—99.5 % minimum purity (200 proof).

6. Sampling

6.1 *Gasoline*—(**Warning**—Extremely flammable. Vapors harmful if inhaled.) Samples to be analyzed by this test method shall be obtained using the procedures outlined in Practice D4057.

7. Apparatus, Configurations, and Method Setup

7.1 *Configuration*—Illustrated and discussed in this test method are three configurations used by the laboratories that have participated in the interlaboratory study (ILS). Figs. A1.5 and A1.6 contain graphical representations of these configurations and Table A1.1 provides the method parameters. Valve-based systems for backflushing may be used and such a configuration is displayed in Fig. A1.7 and was also used in the ILS. Other configurations may be used provided all of the requirements and criteria in this test method are met, such as signal to noise (S/N), resolution, calibration, quality control requirements, and so forth, which are discussed in 7.5 and Section 11.

7.1.1 *Configuration A*—Has the capability of monitoring the effluent from the pre-column via a restrictor. This is a dual detector system. One FID is used to monitor the analytical column's effluent, and the other to monitor the effluent from the pre-column. The second FID provides a quicker approach in determining backflush time. Figs. A1.1 and A1.2 represent examples of this configuration.

7.1.2 *Configuration B*—Has the capability of monitoring the effluent from the pre-column via a restrictor; however, only one FID is installed. Figs. A1.3 and A1.4 represent examples of this configuration.

7.1.3 *Configuration C*—Does not have the capability to monitor the effluent from the pre-column. Figs. A1.5 and A1.6 represent an example of this configuration.

7.2 *Conditioning Column*—Install the pre-column, analytical column, and the restrictor, if the restrictor is being used as in configurations A and B. Condition the columns per manufacturer's instructions.

7.3 *Determine Time to Backflush (BF)*—Or backflush time, must be empirically determined for each system and column set used by the laboratory. Optimization of backflush time is dependent upon the configuration used.

7.3.1 *Configuration A, Dual Detector Configuration*—Follow the instrument setup as shown in Figs. A1.1 and A1.2.

7.3.1.1 Establish analytical parameters set forth in Table A1.1 or parameters that have met method separation criteria as outlined in 7.5. Ensure both detector channels are being collected by the CDS.

7.3.1.2 Inject 0.1 µL to 0.5 µL of standard #1 (8.2) or the butanol composite mix (8.5.2) depending on ethanol or butanol blended gasoline, respectively. If the gasoline being tested is blended with ethanol and not butanol, the composite mix described in 8.5.2 for butanol blend does not need to be prepared. However, if the laboratory wants to prepare this composite mix, the composite mix described in 8.5.2 may be used for establishing backflush time for both blended fuels.

7.3.1.3 Record the time when toluene returns to baseline from the pre-column via the restrictor. A chromatogram from the pre-column through the restrictor demonstrating this is shown in Fig. A1.8 for standard #1, and in Fig. A1.9 for the composite mix in 8.5.2.

7.3.1.4 Next monitor the effluent from the analytical column using the backflush time established in 7.3.1.3. Inject standard #1 (8.2) or composite mix for butanol blend (8.5.2). Record the area for toluene.

7.3.1.5 Reduce the backflush time by 0.02 min. Inject standard #1 or composite mix. Record the area for toluene. Repeat this step until the response for toluene begins to decrease.

7.3.1.6 The backflush time for the method will be the time recorded before the time when toluene decreased. An example chromatogram from the analytical column of standard #1 is in Fig. A1.10 and an example chromatogram of composite mix described in 8.5.2 is located in Fig. A1.11.

7.3.2 *Configuration B, Single Detector Configuration*—To monitor the flow from the pre-column to establish the backflush time, the analytical column is removed from the FID and left in the GC oven as displayed in Fig. A1.3. (**Warning**—Use caution if using hydrogen as carrier gas; if possible, vent externally of the gas chromatograph's oven.) The restrictor is installed into the FID.

7.3.2.1 Follow procedures from 7.3.1.1 through 7.3.1.3.

7.3.2.2 Remove restrictor from the detector and install the analytical column in the detector for analysis as shown in Fig. A1.4.

7.3.2.3 Follow procedures from 7.3.1.4 to 7.3.1.6.

7.3.3 *Configuration C, No Pre-column Configuration*—This configuration is not capable of monitoring the chromatography from the pre-column. An example of this configuration is shown in Figs. A1.5 and A1.6 configuration C.

7.3.3.1 Inject 0.1 µL to 0.5 µL of standard #1 (8.2) or the composite mix (8.5) depending on ethanol or butanol blended gasoline using a backflush time equal to the run-time.

7.3.3.2 Decrease the backflush time by 1 min intervals until toluene is no longer present in the chromatogram.

7.3.3.3 Increase the backflush time by 0.02 min until toluene provides a stable area count. The shortest time when the toluene has a stable response is the backflush time.

7.4 *Re-establishing Backflush Time*—As the column ages with use, retention times will become shorter. If the quality control samples fail, backflush time may need to be re-established on the same column, set especially if a retention time shift is when a new pre-column, analytical column, and/or restrictor are employed, the backflush time will need to be re-established.

7.5 Method Criteria:

7.5.1 *Verify Resolution for Gasoline Blended With Ethanol*—Using the injection volume and other parameters that will be used for sample analysis, inject either composite mix described in 8.5.1 or 8.5.2. Benzene shall be sufficiently resolved from ethanol and having a resolution (R) value >2. The internal standard (MIBK) shall have an R value >1.5. Refer to Fig. A1.10 for standard #1 or Fig. A1.11 for an example chromatogram displaying resolution for composite mix from 8.5.2.

7.5.2 *Verify Resolution for Gasoline Blended With Butanol*—Using the injection volume and parameters established above and that will be used for sample analysis, inject composite mix described in 8.5.2. The resolution requirements are as follows: benzene R > 2; MIBK R > 1.5; toluene R > 0.6. Refer to an example chromatogram found in Fig. A1.11.

7.5.3 Resolution calculation may be performed by the CDS or manually. If using a CDS, ensure the CDS is using the proper resolution calculation, as follows:

$$R_{p2} = \frac{1.18(T_{p2} - T_{p1})}{W_{h1/2} + W_{h2/2}} \quad (1)$$

where:

- R_{p2} = the resolution of peak 2,
- T_{p1} = the retention time of peak 1,
- T_{p2} = the retention time of peak 2,
- $W_{h1/2}$ = the width of peak 1 at half height, and
- $W_{h2/2}$ = the width of peak 2 at half height.

7.5.4 *Determining Method Run Time or Completion of Chromatography for Butanol Blended Gasoline*—Because *n*-butanol may be an isomer in the butanol blend, the runtime and/or temperature needs to be long enough and temperature high enough to ensure *n*-butanol elutes from the analytical column. Use the composite mix in 8.5.2 for this determination. Refer to the chromatogram found in Figs. A1.10 and A1.11.

7.5.5 *Attaining Detection Limit for Benzene*—Using standard mix #7 (8.1), ensure that at least a signal to noise of 50 to 1 is attained for benzene. If this is not achieved, reduce the instrument's split flow or increase the injection volume, not to exceed 0.5 µL until this criteria is attained.

7.5.6 *Calibration Requirements*—A linear regression, or weighted curve, shall meet a criterion correlation coefficient equal to or greater than 0.999.

8. Calibration and Standardization

8.1 *Standards*—Prepare seven standards (Table 1) covering the range 0.06 % to 5 % by volume benzene and 0.5 % to 20 % by volume toluene. For each standard, measure the volume of benzene and of toluene listed below into a 100 mL volumetric flask. Dilute to volume with *isooctane* (2,2,4-trimethylpentane), with all components and glassware at ambient temperature.

8.2 *Final Standard Preparation*—Accurately measure 1.0 mL of MIBK into a 25 mL-volumetric flask, and fill to the mark using the first standard (8.1). Continue doing this until all seven (7) blends (concentrations) have been prepared.

NOTE 4—Commercially prepared calibration standards may be used, including those that are pre-mixed with the MIBK internal standard. The purity of target compounds is given in 5.12.

8.3 *Chromatographic Analysis*—Chromatograph each of the calibration blends using the conditions established in Section 7 using the automated sampling system of the gas chromatograph.

8.4 *Calibration*—Using a computer data system (CDS), measure the area of the benzene and toluene aromatic peaks and of the internal standard peak. Calculate the area ratio of the benzene peak area to the MIBK peak area. Plot the concentration of benzene versus the area ratio. Make the same calculation and plot similarly for toluene. Refer to Fig. A1.12 for an example calibration curve. The calibration shall be linear with a correlation coefficient greater than or equal to 0.999. Weighing the calibration curve 1/y is allowed and will provide enhanced accuracy for lower concentration target samples.

NOTE 5—Some CDS systems plot the area ratio versus the concentration ratio of the benzene and toluene to that of the internal standard. Consult the system guidelines.

8.5 *Composite Mix for Ethanol and Butanol Blends*—The composite mix will ensure a necessary separation of ethanol from benzene (R > 2), and that possible contaminants in the butanol blend will not co-elute with benzene (R > 2), toluene (R > 0.6) and MIBK (R > 1.5).

8.5.1 *Composite Mix for Ethanol Blend*—Prepare a solution by volume that is 20 % ethanol, 1 % benzene, 4 % MIBK and 20 % toluene in *iso*-octane. This solution may also be used to determine the backflush time.

8.5.2 *Composite Mix for Ethanol and Butanol Blends*—Prepare a solution by volume that is 20 % ethanol, 1 % benzene, 4 % *sec*-butanol, 0.1 % *n*-propanol, 4 % MIBK, 20 % toluene, 20 % *iso*-butanol, 5 % *n*-butanol in *iso*-octane. This solution may also be used to determine the backflush time.

TABLE 1 Seven Standards

Std #	Benzene		Toluene	
	Volume percent	mL	Volume percent	mL
1	5	5	20	20
2	2.5	2.5	15	15
3	1.25	1.25	10	10
4	0.67	0.67	5	5
5	0.33	0.33	2.5	2.5
6	0.12	0.12	1	1
7	0.06	0.06	0.5	0.5

9. Procedure

9.1 *Preparation of Sample*—Accurately measure 1.0 mL of MIBK into a 25 mL volumetric flask. Fill to the mark with the sample to be analyzed and mix well.

9.2 *Chromatographic Analysis*—Chromatograph the sample, using the conditions established in Section 7 and as used for the calibration. The GC column flow must be turned to backflush mode at the time determined in 7.2 so that undesirable components do not enter the analytical column. Fig. A1.13 is an example of a Test Method D3606 proficiency sample analyzed using configuration A.

9.3 *Interpretation of Chromatogram*—Identify the benzene, toluene, and the internal standard MIBK peaks from the retention times of the standards.

NOTE 6—The order of elution will be nonaromatic hydrocarbons, benzene, MIBK and toluene using the dimethyl poly siloxane and polar column combination used in the ILS.

9.4 *Measurement of Area*—Measure the areas under the benzene, toluene aromatic peaks and under the MIBK peak.

10. Calculation

10.1 Calculate the ratios of the peak areas of benzene and toluene to the peak area of MIBK. Determine from the calibration curve the liquid volume percent of benzene and toluene corresponding to the calculated peak ratios. A CDS that has the capability of processing this calibration and quantitative results may be used.

10.2 If the results are desired on a mass basis, convert to mass percent as follows:

$$\text{Benzene, mass percent} = (V_B / D) \times 0.8844 \quad (2)$$

where:

V_B = volume percent benzene, and

D = relative density of sample at 15.6/15.6 °C (60/60 °F).

$$\text{Toluene, mass percent} = (V_T / D) \times 0.8719 \quad (3)$$

where:

V_T = volume percent toluene, and

D = relative density of sample at 15.6/15.6 °C (60/60 °F).

11. Quality Control

11.1 *Test for System Stability and Repeatability*—On setting up the method for the first time and thereafter when major maintenance is performed (change in columns and flows, for example), make six injections of standard #4 (8.2). Calculate the standard deviation from the six results from the six injections. Calculate $2.77 \times$ the standard deviation obtained. This quantity shall meet repeatability as published 13.1.1. Thereafter establish statistical quality control charting (SQC) for each batch of analysis analyzed using a production sample similar in composition to samples to be analyzed.

11.2 *Reference Material*—Analyze one or more reference material of known accepted reference value (ARV), such as from NIST and/or an independent certified control standard, or meeting the check standard requirement as specified in Practice D6299 upon setting up the test method, post maintenance (calibration, column replacement, cut time adjustments, and so

forth) and at least quarterly to confirm proper set-up and calibration of the gas chromatograph. Test results shall agree with within the 95 % confidence level or reproducibility of the benzene or toluene components divided by the square root of 2. In addition follow any other specification requirements per regulatory or commercial application(s). Monitor the performance of the reference material(s) using SQC charting in accordance with Practice D6299.

12. Report

12.1 Report the benzene and toluene contents in liquid volume percent to the nearest 0.01 %, and indicate that the results are from “D3606 Procedure A.”

13. Precision and Bias³

13.1 The following criteria should be used for judging the acceptability of results (95 % confidence). The user should choose the precision statement that reflects the concentration range of each component under study.

13.1.1 *Repeatability*—The difference between two independent results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would exceed the values in Table 2 with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method.

13.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would exceed the values in Table 3 with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method.

NOTE 7—The sample compositions and results of the cooperative study are filed at ASTM International.

13.2 *Bias*—Since there is no accepted reference method suitable for measuring bias for this method, no statement of bias can be made.

13.2.1 *Relative Bias between Procedure A and Procedure B for Benzene:*

13.2.1.1 A relative bias assessment of Test Method D3606 Procedure A versus Procedure B for the determination of benzene in spark-ignition fuel (gasolines) was conducted using data from the ILS of Procedure A which also included a parallel

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-2004. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Repeatability—Procedure A (WCOT Column)

NOTE 1— X = the average of two results in volume percent of the component; each result is to be within the ranges below.

Component	Inclusive Valid Test Result Range, Volume percent (see Table 7)	Repeatability
Benzene	0.07 to 5.96	0.03202 ($X + 0.2$)
Toluene	0.36 to 20.64	0.01767 ($X + 0.5$)

TABLE 3 Reproducibility—Procedure A (WCOT Column)

NOTE 1—X = the average of two results in volume percent of the component; each result is to be within the ranges given below.

Component	Inclusive Valid Test Result Range, volume percent (see Table 7)	Reproducibility
Benzene	0.07 to 5.96	0.1462 (X + 0.2)
Toluene	0.36 to 20.64	0.04659 (X + 0.5)

TABLE 4 Repeatability/Reproducibility Example (Benzene)—Procedure A (WCOT Column)

Benzene Volume percent	Repeatability	Reproducibility
0.1	0.010	0.044
0.2	0.013	0.058
0.3	0.016	0.073
0.4	0.019	0.088
0.5	0.022	0.102
0.6	0.026	0.117
0.7	0.029	0.132
0.8	0.032	0.146
0.9	0.035	0.161
1.0	0.038	0.175
2.0	0.070	0.322
3.0	0.102	0.468
4.0	0.134	0.614
5.0	0.167	0.760

TABLE 5 Repeatability/Reproducibility Example (Toluene)—Procedure A (WCOT Column)

Toluene Volume percent	Repeatability	Reproducibility
0.4	0.016	0.042
1.0	0.027	0.070
2.0	0.044	0.116
3.0	0.062	0.163
4.0	0.080	0.210
5.0	0.097	0.256
6.0	0.115	0.303
7.0	0.133	0.349
8.0	0.150	0.396
9.0	0.168	0.443
10.0	0.186	0.489
11.0	0.203	0.536
12.0	0.221	0.582
13.0	0.239	0.629
14.0	0.256	0.676
15.0	0.274	0.722
16.0	0.292	0.769
17.0	0.309	0.815
18.0	0.327	0.862
19.0	0.345	0.909
20.0	0.362	0.955

ILS using Procedure B using identical samples. The assessment was performed in accordance with the requirements of Practice D6708 with a successful outcome and is documented in Research Report RR:D02-2004.³

NOTE 8—Procedure B is based on the original version of D3606 which uses packed columns and which has been used by regulatory agencies for benzene. Users of this D3606 test method should consult proper regulations on its use as regulations may change.

13.2.1.2 The degree of agreement between results from Test Method D3606 Procedure A versus Procedure B can be further improved by applying a correlation equation (Eq 4) (Research

TABLE 6 Comparison of Precision between Procedure A and Procedure B in the Range of 0.10 % to 1.5 % Volume for Benzene

Benzene percent volume	Procedure A		Procedure B	
	Repeatability	Reproducibility	Repeatability	Reproducibility
0.10	0.010	0.044	0.013	0.063
0.30	0.016	0.073	0.019	0.089
0.50	0.022	0.102	0.025	0.115
0.70	0.029	0.132	0.031	0.141
0.90	0.035	0.161	0.037	0.167
1.10	0.042	0.190	0.043	0.193
1.30	0.048	0.219	0.049	0.219
1.50	0.054	0.249	0.055	0.245

Report RR:D02-2004³). There were no discernable sample-specific biases as determined by D6708.

13.2.1.3 *Correlation Equation:*

13.2.1.4

Predicted D3606 Procedure B benzene

$$= \text{bias corrected Procedure A benzene} = C_{\text{procedure A}} + 0.017 \quad (4)$$

where:

$C_{\text{procedure A}}$ = volume percent benzene as reported by Test Method D3606 Procedure A.

(1) The correlation equation is applicable to test results in the range of 0.07 % to 5.96 % by volume as obtained using Test Method D3606 Procedure A.

(2) To predict the Test Method D5769 value of benzene from D3606 Procedure A, first convert Procedure A test result to Procedure B test result (Eq 4) and then use the correlation equation and instructions in the relative bias section 26.2.1 of Procedure B to convert the obtained Procedure B value to the Test Method D5769 test result.

13.2.2 *Relative Bias between Procedures A and B Toluene:*

13.2.2.1 A relative bias assessment of Test Method D3606 Procedure A versus Procedure B for the determination of toluene was conducted using data from the ILS of Procedure A which also included a parallel ILS using Procedure B using identical samples. The assessment was performed in accordance with the requirements of Practice D6708 with a successful outcome and is documented in Research Report RR:D02-2004.³

13.2.2.2 The degree of agreement between results from Test Method D3606 Procedure A toluene versus Procedure B toluene can be further improved by applying a correlation equation (Eq 5) (Research Report RR:D02-2004³). There were no discernable sample-specific biases as defined in Practice D6708.

13.2.2.3 *Correlation Equation:*

13.2.2.4

Predicted D3606 Procedure B toluene

$$= \text{bias corrected Procedure A toluene} = 1.01 * C_{\text{Procedure A}} - 0.025 \quad (5)$$

where:

$C_{\text{Procedure A}}$ = volume percent toluene as reported by Test Method D3606 Procedure A.

TABLE 7 Valid Test Result Ranges for Benzene and Toluene

NOTE 1—Due to testing variation, results within the following ranges inclusively are considered valid for reporting and for applying the precision functions per Practice D6300.

Compound Volume Percent	Lowest Mean ^A	Highest Mean ^A	R_lowest	R_highest	D3606 Procedure A Valid Test Result Range ^B
Benzene: D3606 Procedure A valid test reporting range	0.12	5.2	0.05	0.76	0.07 to 5.96
Benzene: D3036 Procedure A valid test result range for Eq 4 (based on mean low and high sample data range used for correlation)	0.12	5.2	0.05	0.76	0.07 to 5.96
Toluene: D3606 Procedure A valid test result reporting range	0.40	19.7	0.04	0.94	0.36 to 20.64
Toluene: D3606 Procedure A valid test result range for equation 5 (based on mean low and high sample data range used for correlation)	0.40	19.7	0.04	0.96	0.36 to 20.64

^A Method working range:

high expected concentration limit – estimated using highest ILS sample mean

low expected concentration limit – estimated using lowest ILS sample mean

^B Valid test result range: due to testing variation, results within this range inclusively are considered valid for reporting and for applying the precision (R and r) functions:

• high limit : highest ILS sample mean + R_{highest} ILS sample mean (per D6300)

• low limit : lowest ILS sample mean – R_{lowest} ILS sample mean (per D6300)

(1) The correlation equation is applicable to test results determined by Test Method D3606 Procedure A in the range of 0.36 % to 20.64 % by volume toluene.

14. Keywords

14.1 aviation gasoline; benzene; gas chromatography; gasoline; multidimensional gas chromatography; spark ignition fuels; toluene

PROCEDURE B—PACKED GAS CHROMATOGRAPHIC COLUMNS

15. Summary of Test Method

15.1 An internal standard, *sec*-butanol, is added to the sample. The sample is then introduced into a gas chromatograph (GC) equipped with two packed GC columns connected in series. The sample passes first through a pre-column packed with a nonpolar or equivalent phase, which separates the lighter components according to boiling point. After toluene has eluted, the flow through the nonpolar column is reversed, flushing out the components heavier than toluene. The lighter components then pass through an analytical column packed with a stationary phase capable of separating benzene and toluene from ethanol and other hydrocarbons and oxygenates such as methanol, MTBE, TAME, ETBE, and butanols. The eluted components are detected by a thermal conductivity detector (TCD). The detector response is recorded, the peak areas are measured and the concentration of each component is calculated with reference to the internal standard.

16. Significance and Use

16.1 Knowledge of the concentration of benzene may be required for regulatory use, control of gasoline blending, and/or process optimizations.

17. Apparatus

17.1 *Chromatograph*—Any multidimensional packed column gas chromatographic instrument configuration that has a backflush system and thermal conductivity detector, and that can meet the specification of this test method, such as column resolution, can be used.

17.1.1 Two backflush systems are shown. Fig. A2.1 is a switching valve system and Fig. A2.2 is a pressure system. Either one can be used.

17.2 Columns:

17.2.1 *Columns A (Precolumn) and B (Analytical Column)*—Annex A2.2 gives an example of a commercial column set that has been used successfully for samples containing ethanol. In addition, Annex A2.4 gives an additional column set originally proposed by the U.S. Environmental Protection Agency (EPA) that may be adequate for this analyses. Other packed column sets that give a resolution from ethanol as specified in 20.3 may be used.

17.3 *Chromatography Data System (CDS)*—An electronic device capable of graphical presentation and integration of the chromatogram peaks.

17.4 *Microsyringe*—5 µL capacity.

17.5 *Volumetric Pipets, Class A*—0.5 mL, 1 mL, 5 mL, 10 mL, 15 mL, and 20 mL capacities (see Specifications E694 and E969).

17.6 *Measuring Pipets*—1 mL and 2 mL capacities calibrated in 0.01 mL; 5 mL calibrated in 0.1 mL, for use in dispensing volumes of benzene and toluene not covered by the volumetric pipets (see Specifications E1044 and E1293) during preparation of standard samples.

NOTE 9—Other volume dispensing equipment capable of delivering the specified volumes within the stated tolerance limits may be used as an alternative to the requirements stated in 17.5 and 17.6.

17.7 *Flasks*—Class A volumetric (see Specification E288), 25 mL and 100 mL capacity.

18. Materials

18.1 *Carrier Gas*—Helium, 99.99 % mol pure or better. (**Warning**—Compressed gas under high pressure.)

18.2 *Solvents*:

18.2.1 *Methanol*—Reagent grade. (**Warning**—Flammable. Vapor harmful. Can be fatal or cause blindness if swallowed or inhaled.)

18.3 *Internal Standard*:

18.3.1 *sec-butanol*—99.5 % mol minimum purity. Free of benzene and toluene. (**Warning**—Flammable. Vapor can be harmful.)

18.4 *Calibration Standards*:

18.4.1 *Benzene*—99+ % mol. (**Warning**—Poison. Carcinogen. Harmful or fatal if swallowed. Extremely flammable. Vapors can cause flash fires.)

18.4.2 *Isooctane (2,2,4-trimethyl pentane)*—99+ % mol. (**Warning**—Extremely flammable. Harmful if inhaled.)

18.4.3 *Toluene*—(**Warning**—Flammable. Vapor harmful.)

18.4.4 *n-nonane*—99+ % mol. (**Warning**—Flammable. Vapor harmful.)

19. Sampling

19.1 *Spark Ignition Fuel (for example, “Gasoline”)*—(**Warning**—Extremely flammable. Vapors harmful if inhaled.) Samples to be analyzed by this test method shall be obtained using the procedures outlined in Practice D4057.

20. Configuration of Apparatus and Establishment of Conditions

20.1 Following manufacturer’s guidelines and/or suggested details in A2.2, A2.3, and A2.4 optimize the chromatographic system.

20.1.1 *Column System Setup for Valve Backflushing*—The following procedure provides a general guideline for optimizing a system using valve switching as shown in Fig. A2.1. Several operational conditions are given in Table A2.1.

20.1.1.1 Set the valve in the *forward flow* mode with columns A and B in series (Fig. A2.2), and adjust the primary flow control to give the desired flow. Measure the flow rate at the detector vent, sample side.

20.1.1.2 Set the valve in the *backflush* position, measure the flow rate at the detector vent, sample side. If the flow has changed, adjust the secondary or auxiliary flow control to obtain the correct flow. Flows should match to within $\pm 1 \text{ cm}^3/\text{min}$.

20.1.1.3 Change the valve from *forward flow* to the *backflush* position several times and observe the baseline. There should be no baseline shift or drift after the initial valve kick that results from the pressure surge. If there is a baseline shift, increase or decrease the secondary flow control slightly to balance the baseline. A persistent drift could indicate leaks somewhere in the system.

20.2 *Determine Time to Backflush*—The time to backflush will vary for each column system and must be determined

experimentally as follows. Table A2.1 gives examples of backflush times. Prepare a mixture of 5 % by volume *isooctane* in *n-nonane*. With the valve configuration in the *forward flow* mode, inject 1 μL of the *isooctane-n-nonane* mixture. Allow the chromatogram to run until the *n-nonane* has eluted and the detector signal has returned to baseline. Measure the time in seconds, from the injection until the detector signal returns to baseline between the *isooctane* and *n-nonane* peaks. At this point all of the *isooctane*, but essentially none of the *n-nonane*, should have eluted. Repeat the run, including the injection, but switching the system to the *backflush* mode at the predetermined “time to backflush.” This should result in a chromatogram of *isooctane* with little or no *n-nonane* visible. If necessary, make additional runs, adjusting the “time to backflush” until this condition of all the *isooctane* and little or no *n-nonane* is attained. The “time to backflush” so established, including the *actual valve operations*, must be used in all subsequent calibrations and analyses. It is also valid to set backflush time after toluene elutes.

20.3 *Resolution of Ethanol/Benzene and Sec-butanol Benzene Pairs*—Resolution calculation may be performed by the CDS or manually. The resolution shall be greater than 1.5 using calibration standard 4 (Table 8) for benzene. If using a CDS, ensure the CDS is using the proper resolution calculation, as follows:

$$R_{p2} = \frac{1.18(T_{p2} - T_{p1})}{W_{h1/2} + W_{h2/2}} \quad (6)$$

where:

R_{p2} = the resolution of peak 2,
 T_{p1} = the retention time of peak 1,
 T_{p2} = the retention time of peak 2,
 $W_{h1/2}$ = the width of peak 1 at half height, and
 $W_{h2/2}$ = the width of peak 2 at half height.

20.4 To ensure proper resolution at low concentration ranges, the ethanol needs to have minimal peak tailing. A2.2 and A2.4 describe the recommended peak symmetry for ethanol and the ethanol/benzene resolution required. It is recommended that final system optimization be verified against certified reference materials containing benzene at several concentration levels of interest and ethanol present at a level in the expected samples to confirm the accuracy of the analyses.

21. Calibration and Standardization

21.1 *Standard Samples*—Prepare seven standard samples (Table 8) covering the range 0.06 % to 5 % by volume benzene and 0.5 % to 20 % by volume toluene as follows: For each

TABLE 8 Seven Standard Samples

Std #	Benzene		Toluene	
	Volume %	mL	Volume %	mL
1	5	5	20	20
2	2.5	2.5	15	15
3	1.25	1.25	10	10
4	0.67	0.67	5	5
5	0.33	0.33	2.5	2.5
6	0.12	0.12	1	1
7	0.06	0.06	0.5	0.5

standard, measure the volume of benzene and of toluene listed below into a 100 mL volumetric flask. Dilute to volume with *isooctane* (2,2,4-trimethyl pentane), with all components and glassware at ambient temperature.

21.2 Calibration Blends—Accurately measure 1.0 mL of *sec*-butanol into a 25 mL volumetric flask, and fill to the mark with the first standard sample (21.1). Continue doing this until all blends have been prepared.

NOTE 10—Commercially prepared calibration standards may be used, including those that are pre-mixed with the *sec*-butanol internal standard.

21.3 Chromatographic Analysis—Chromatograph each of the calibration blends using the conditions established in 20.4 using the following injection technique:

21.4 Injection of Sample:

21.4.1 Use an automatic liquid sample injection system. If manual injections are to be made, the injection technique in 21.4.2 is necessary so that sharp symmetrical peaks will be obtained.

NOTE 11—ILS precision was based using automated injection systems.

21.4.2 Flush the 5 µL microsyringe at least three times with the sample mixture and then fill with about 3 µL of the sample. (Avoid including any air bubbles in the syringe). Slowly eject the sample until 2.0 µL remains in the syringe; wipe the needle with tissue and draw back the plunger to admit 1 µL to 2 µL of air into the syringe. Insert the needle of the syringe through the septum cap of the chromatograph and push until the barrel of the syringe is resting against the septum cap; then push the plunger to the hilt and remove the syringe immediately from the chromatograph.

21.5 Calibration—Measure the area of both aromatic peaks and of the internal standard peak. Calculate the ratio of the benzene peak area to the *sec*-butanol and the ratio of concentrations of benzene to that of the *sec*-butanol. Plot the area ratios versus and concentration ratios. Make the same calculation and plot for toluene. The calibrations shall be linear (Fig. A2.6).

NOTE 12—Some CDS systems plot the area ratio versus the concentration ratio of the benzene and toluene to that of the internal standard. Consult the system guidelines.

22. Procedure

22.1 Preparation of Sample—Accurately measure 1.0 mL of *sec*-butanol into a 25 mL volumetric flask. Fill to the mark with the sample to be tested and mix well.

22.2 Chromatographic Analysis—Chromatograph the sample, using the conditions established in Section 20 “time to backflush” and the injection technique described in 21.4. The valves must be turned to backflush mode at the time determined in 20.2 so that undesirable components do not enter Column B.

22.3 Interpretation of Chromatogram—Identify on the chromatogram the benzene, toluene, and the internal standard *sec*-butanol peaks from the retention times of the standards.

NOTE 13—The order of elution will be nonaromatic hydrocarbons, ethanol, benzene, *sec*-butanol, and toluene using the prescribed column system in A2.2. Figs. A2.5 and A2.6 are examples of typical chromatograms.

22.4 Measurement of Area—Measure the areas under the aromatic peaks and under the internal standard peak by CDS.

NOTE 14—The precision statement in Section 25 was developed from data obtained using electronic integrators or on-line computers. The precision statement may not apply if other methods of integration or peak area measurement are used.

23. Calculation

23.1 Calculate the ratios of the peak areas of benzene and toluene to the peak area of the internal standard or if using concentration ratios also ratio of benzene and aromatics to that of the internal standard. Determine from the appropriate calibration curve the liquid volume percent of benzene and toluene corresponding to the calculated peak ratios.

23.2 If the results are desired on a mass basis, convert to mass percent as follows:

$$\text{Benzene, mass percent} = (V_B / D) \times 0.8844 \quad (7)$$

where:

V_B = volume percent benzene, and

D = relative density of sample at 15.6/15.6 °C (60/60 °F).

$$\text{Toluene, mass percent} = (V_T / D) \times 0.8719 \quad (8)$$

where:

V_T = volume percent toluene, and

D = relative density of sample at 15.6/15.6 °C (60/60 °F).

24. Report

24.1 Report the benzene and toluene contents in liquid volume percent to the nearest 0.01 %. Indicate that result is from “D3606 Procedure B.”

25. Quality Control

25.1 Test for System Stability and Repeatability—On setting up the method for the first time and thereafter when major maintenance (change in columns and flows, for example) is performed, make six injections of standard #4 (Table 8). Calculate the standard deviation from the six results from the six injections. Calculate $2.77 \times$ the standard deviation obtained. This quantity shall meet repeatability as published in 26.1.1. Thereafter, establish statistical quality control charting (SQC) for each batch of analysis analyzed using a production sample similar in composition to samples to be analyzed.

25.2 Reference Material—Analyze one or more reference material of known accepted reference value (ARV), such as from NIST and/or an independent certified control standard, or meeting the check standard requirement as specified in Practice D6299 upon setting up the test method, post maintenance (calibration, column replacement, cut time adjustments, and so forth) and at least quarterly to confirm proper set-up and calibration of the gas chromatograph. Test results shall agree with within the 95 % confidence level or reproducibility of the benzene or toluene components divided by the square root of 2. In addition follow any other specification requirements per regulatory or commercial application(s). Monitor the performance of the reference material(s) using SQC charting in accordance with Practice D6299.

26. Precision and Bias

26.1 The following criteria should be used for judging the acceptability of results (95 % confidence). The user should choose the precision statement that reflects the concentration range of each component under study.

26.1.1 *Repeatability*—The difference between two independent results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would exceed the values in **Table 9** with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method.

26.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would exceed the values in **Table 10** with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method:

NOTE 15—In order to reflect changes in gasoline composition, the precision for this test method was determined in 1994 using both conventional gasolines as well as gasolines containing oxygenates (ethers such as methyl *tert*-butyl ether, ethyl *tert*-butyl ether, and *tert*-amyl methyl ether, and alcohols such as ethanol). This precision should be used when the concentration of benzene (0.1 % to 1.5 % by volume) and toluene (1.7 % to 9 % by volume) fall within the specified range. The sample composition and results of the cooperative study are filed at ASTM International.⁴

NOTE 16—The precision was determined using conventional motor gasolines without oxygenates and purchased on the open market. This precision should be used when the concentration of benzene exceeds 1.5 % by volume and toluene 9 % by volume. The sample compositions and results of the cooperative study are filed at ASTM International.⁴

26.2 *Bias*—Since there is no accepted reference method suitable for measuring bias for this test method, no statement of bias can be made.

26.2.1 *Relative Bias*—A relative bias assessment of Test Method D3606 Procedure B versus Test Method **D5769** for the determination of benzene in spark-ignition fuel was conducted using data from the ASTM D02 Interlaboratory Crosscheck Program. The assessment was performed in accordance with the requirements of Practice **D6708** with a successful outcome. It was based on measurements of benzene in spark-ignition engine fuels supplied between January 2006 and October 2014 by the Reformulated Gasoline program of the ASTM Profi-

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1042. Contact ASTM Customer Service at service@astm.org.

TABLE 9 Repeatability Benzene/Toluene (Procedure B)

NOTE 1— X = the average of two results in volume percent of the component; each result is to be within the ranges given below.

Component	Inclusive Valid Reporting Range, Volume percent (see Table 13)	Repeatability	See Note
Benzene	0.04 to 1.5	$0.03(X) + 0.01$	Note 15
Benzene	>1.5 to 5.25	0.03	Note 16
Toluene	1.7 to 9	$0.03(X) + 0.02$	Note 15
Toluene	>9 to 21.15	0.62	Note 16

TABLE 10 Reproducibility Benzene/Toluene (Procedure B)

NOTE 1— X = the average of two results in volume percent of the component; each result is to be within the ranges given below.

Component	Inclusive Valid Reporting Range, Volume percent (see Table 13)	Reproducibility	See Note
Benzene	0.04 to 1.5	$0.13(X) + 0.05$	Note 15
Benzene	>1.5 to 5.25	0.28	Note 16
Toluene	1.7 to 9	$0.12(X) + 0.07$	Note 15
Toluene	>9 to 21.15	1.15	Note 16

TABLE 11 Repeatability/Reproducibility Example (Benzene)—Procedure B (Packed Column)

Concentration Volume percent	r	R
0.1	0.01	0.06
0.2	0.02	0.08
0.3	0.02	0.09
0.4	0.02	0.10
0.5	0.03	0.12
0.6	0.03	0.13
0.7	0.03	0.14
0.8	0.03	0.15
0.9	0.04	0.17
1.0	0.04	0.18
1.5	0.06	0.25
2.0	0.03	0.46
3.0	0.03	0.69
4.0	0.03	0.92
5.0	0.03	1.15

TABLE 12 Repeatability/Reproducibility Example (Toluene)—Procedure B (Packed Column)

Concentration Volume percent	r	R
1.7	0.07	0.27
2.0	0.08	0.31
3.0	0.11	0.43
4.0	0.14	0.55
5.0	0.17	0.67
6.0	0.20	0.79
7.0	0.23	0.91
8.0	0.26	1.03
9.0	0.29	1.15
10.0	0.62	1.15
11.0	0.62	1.15
12.0	0.62	1.15
13.0	0.62	1.15
14.0	0.62	1.15
15.0	0.62	1.15
16.0	0.62	1.15
17.0	0.62	1.15
18.0	0.62	1.15

ciency Testing Program (Interlaboratory Crosscheck Program) and is documented in Research Report RR:D02-1816.⁵ The correlation meets the requirements per EPA's Performance Based Measurement System (PBMS).

NOTE 17—There is an allowance in the EPA (PBMS) regulation to use other test methods if they are formally correlated with the specified test method by a consensus organization, for example, ASTM. This relative

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1816. Contact ASTM Customer Service at service@astm.org.

bias statement is intended to satisfy the requirement of PBMS and allow use of Test Method D3606 Procedure B bias corrected results in the stated concentration ranges in place of Test Method D5769 for benzene. Regulations and specified test methods may change, the user should consult current regulations on use of such test methods.

26.2.1.1 The degree of agreement between results from Test Method D3606 Procedure B and Test Method D5769 can be further improved by applying a correlation equation (Eq 9) (Research Report RR:D02-1816).⁵ There were no discernible sample-specific biases as defined in D6708.

26.2.1.2 *Correlation Equation:*

26.2.1.3

$$\text{Predicted D5769} = \text{bias corrected D3606 Procedure B} = C_{3606B} - 0.01 \quad (9)$$

where:

C_{3606B} = volume percent benzene as reported by Test Method D3606 Procedure B.

(1) The correlation equation is applicable for fuels (gasolines) that when determined by Test Method D3606 Procedure B are in the concentration range of 0.04 % to 2.53 % by volume. See Table 13.

NOTE 18—The Test Method D3606 Procedure B concentration range used to develop the Practice D6708 assessment may not cover the entire concentration range indicated in the scope of Test Method D3606 Procedure B for benzene.

NOTE 19—The correlation equation was developed from a variety of

fuel (gasolines) samples from the ASTM Interlaboratory Crosscheck programs; however, it is recommended that the correlation equation be verified for samples of interest to ensure applicability.

26.2.1.4 *Between Method Reproducibility*—Differences between bias-corrected results from Test Method D3606 Procedure B and Test Method D5769, for the sample types and property ranges studied, are expected to exceed the following (Table 14) between-methods reproducibility (R_{xy}), as defined in Practice D6708 (Research Report RR:D02-1816⁵), about 5 % of the time.

27. Keywords

27.1 aviation gasoline; benzene; ethanol; gas chromatography; gasoline; multidimensional gas chromatography; spark ignition fuel; toluene

TABLE 13 Valid Test Result Ranges for Benzene

NOTE 1—Due to testing variation, results within the following ranges inclusively are considered valid for reporting and for applying the precision functions per Practice D6300.

Benzene percent volume	Lowest Mean ^A	Highest Mean ^A	R_lowest	R_highest	Inclusive Valid Test Result Range ^B for D3606 Procedure B
D3606 Procedure B valid reporting range	0.10	5.0	0.06	0.25	0.04 to 5.25
D3606 Procedure B to D5769 relative bias valid test result range for Eq 9 (based on low and high sample mean used in the correlation)	0.05	2.25	0.01	0.28	0.04 to 2.53

^A Method working range:

high expected concentration limit – estimated using highest ILS sample mean

low expected concentration limit – estimated using lowest ILS sample mean

^B Valid test result range: due to testing variation, results within this range inclusively are considered valid for reporting and for applying the precision (R and r) functions:

• high limit : highest ILS sample mean + $R_{\text{highest ILS sample mean}}$ (per D6300)

• low limit : lowest ILS sample mean – $R_{\text{lowest ILS sample mean}}$ (per D6300)

**TABLE 14 Between Methods Reproducibility for Predicted D5769
from D3606 Procedure B**

Predicted D5769 Volume Percent	Rxy
0.06	0.054
0.09	0.057
0.19	0.067
0.49	0.097
0.70	0.122
0.99	0.148
1.49	0.200
2.49	0.303

ANNEXES

(Mandatory Information)

A1. PROCEDURE A

A1.1 These configurations and operating conditions are approximate and may require optimization for each instrument and configuration. It is possible that configurations of pressure switching and/or valve switching may vary among manufacturers. It is important that all critical parameters such as resolution, calibration linearity, quality control, and so forth be met as specified in this test method. Consult manufacturer for guidance.

A1.2 See Table A1.1 for Operating Conditions—Configuration A.

A1.3 See Figs. A1.1-A1.13 for Example Configurations, Chromatograms, and Calibration.

TABLE A1.1 Operating Conditions—Configuration A (Example From ILS)

Parameter	Configuration A
Pre-Column	Dimethyl Polysiloxane (non-polar): 30 m x 0.25 mm x 0.25 μm
Analytical Column	CarboWax (Polar): 30 m x 0.25 mm x 0.5 μm
Restrictor	42.5 cm x 0.1 mm (no phase)
Flow rate: Pre-Column	Initial: 2.0 mL/min 2.91 min: 1.4 mL/min
Flow rate: Restrictor	Initial: 4.0 mL/min 2.91 min: 3.3 2mL/min
Flow rate: Analytical Column	Initial: 2.6 mL/min 2.91 min: 2.0 mL/min
Inlet Pressure, kPa (psi)	Initial: 151.71 (22.0) 2.91 min: 34.51 (5.0)
Auxillary or Midpoint pressure, kPa (psi)	Initial: 89.6 (13.0) 2.91 min: 75.80 (11.0)
Split Ratio	100:1
Oven Parameters	Initial Temp: 75 °C hold 8 min Temp 2: 85 °C hold 3 min Temp 3: 140 °C hold 0.4 min Ramp 1: 5 °C/min Ramp 2: 40 °C/min
Inlet Temp	200 °C
Detector Temp	200 °C

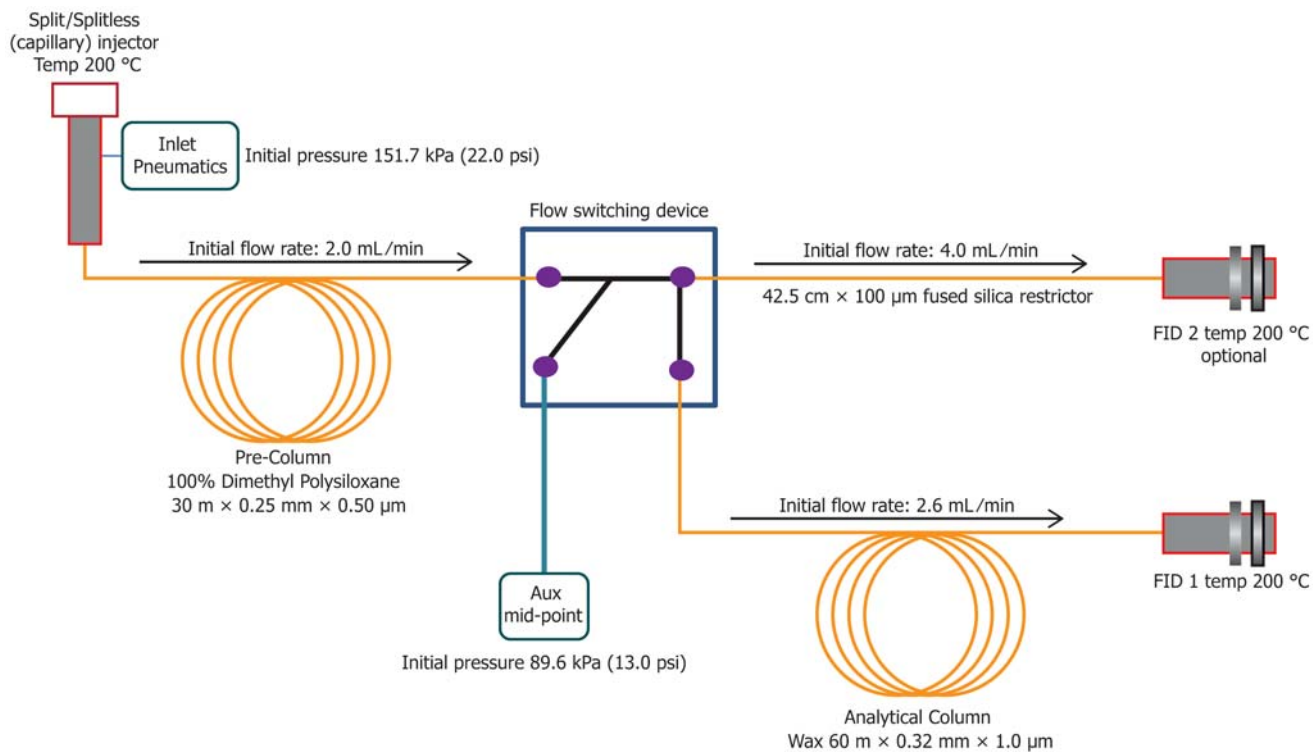


FIG. A1.1 Configuration A—Demonstrates Elution of Sample from Pre-column onto Analytical Column Before Backflush Using Dual Detector Instrument

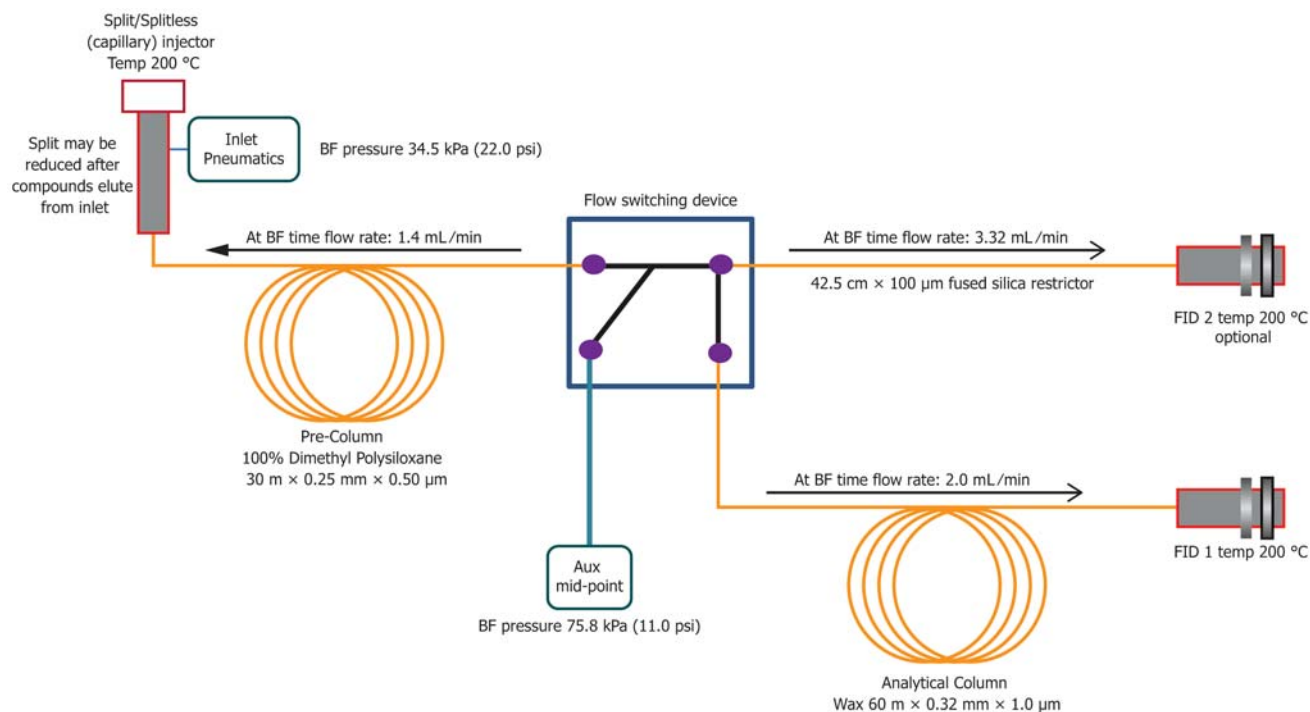


FIG. A1.2 Configuration A—Demonstrates How Backflushing is Accomplished After Elution of Toluene

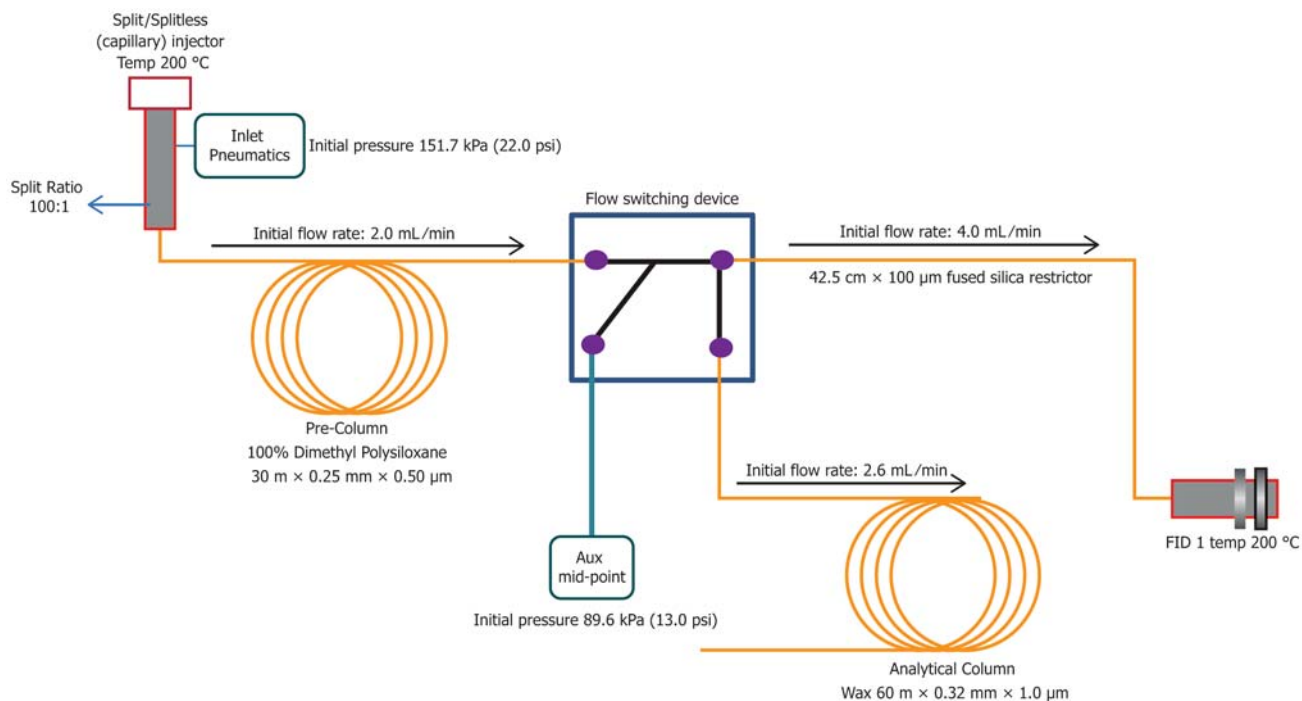


FIG. A1.3 Configuration B—Demonstrates Elution of Sample from Pre-column onto Analytical Column Before Backflush Using Single Detector Instrument

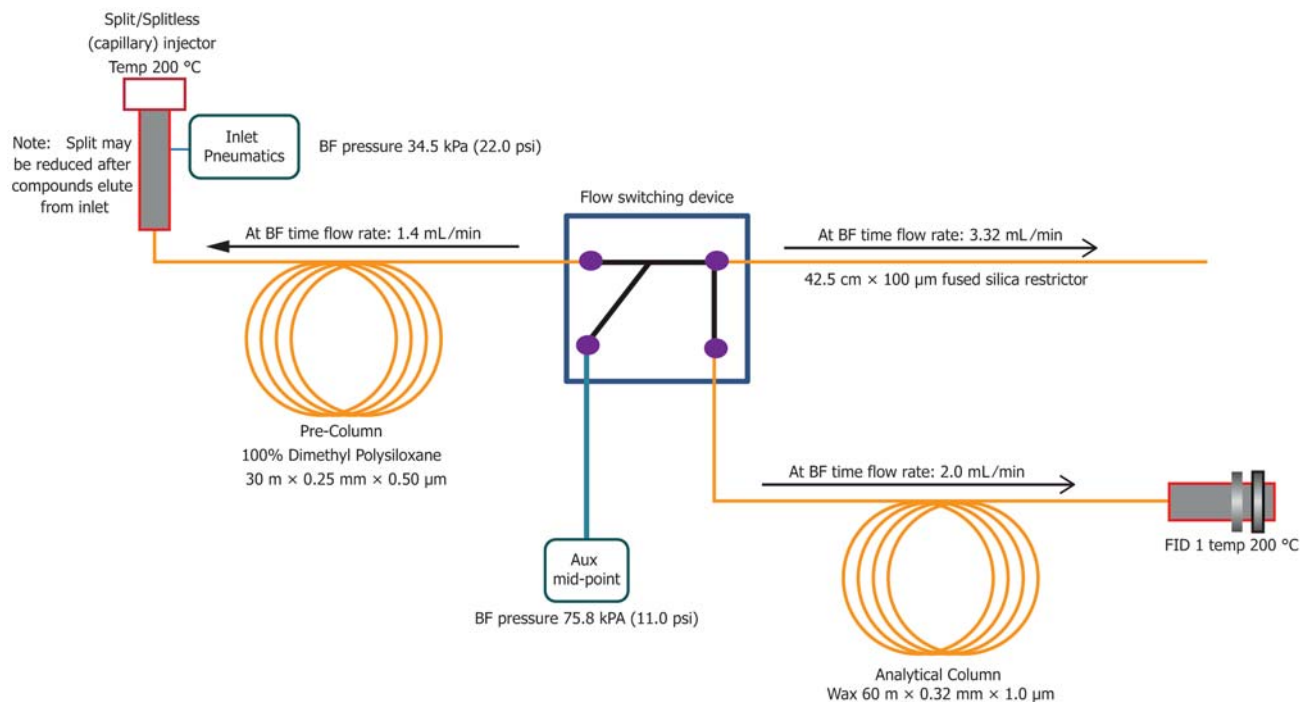


FIG. A1.4 Configuration B—Demonstrates How Backflushing is Accomplished After Elution of Toluene

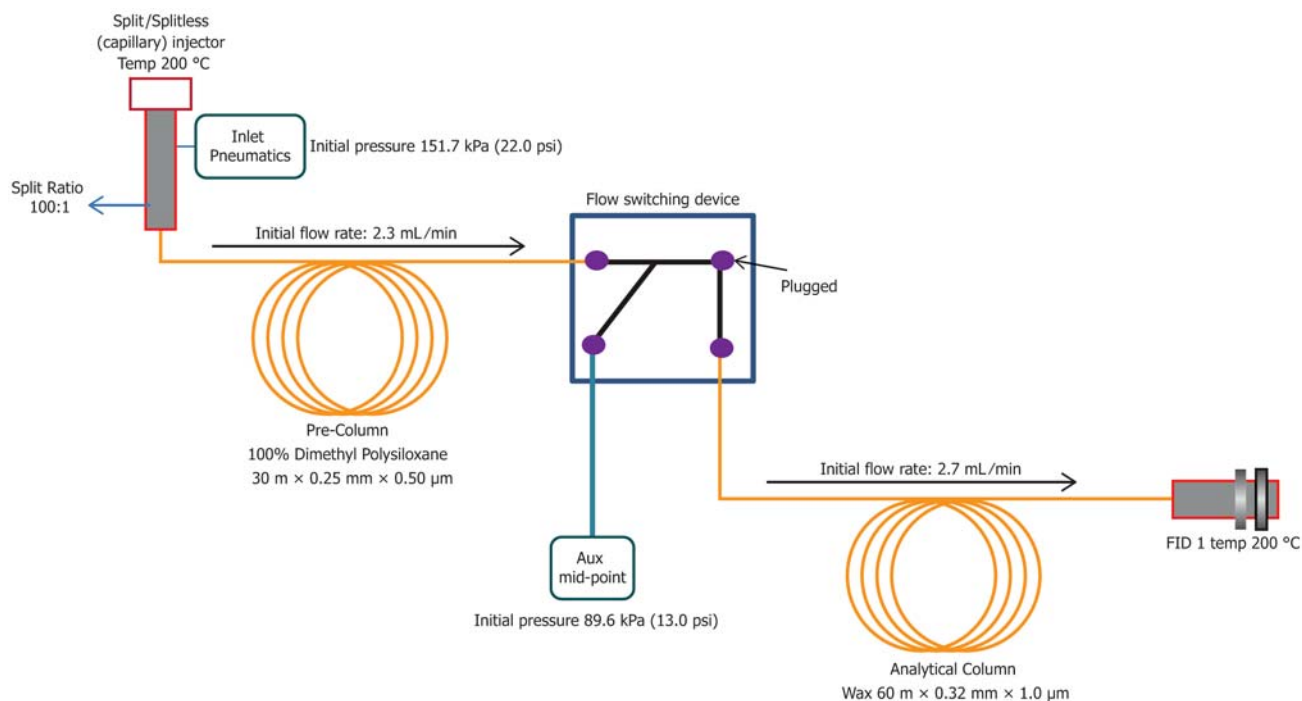


FIG. A1.5 Configuration C—Demonstrates Elution of Sample from Pre-column onto Analytical Column Before Backflush

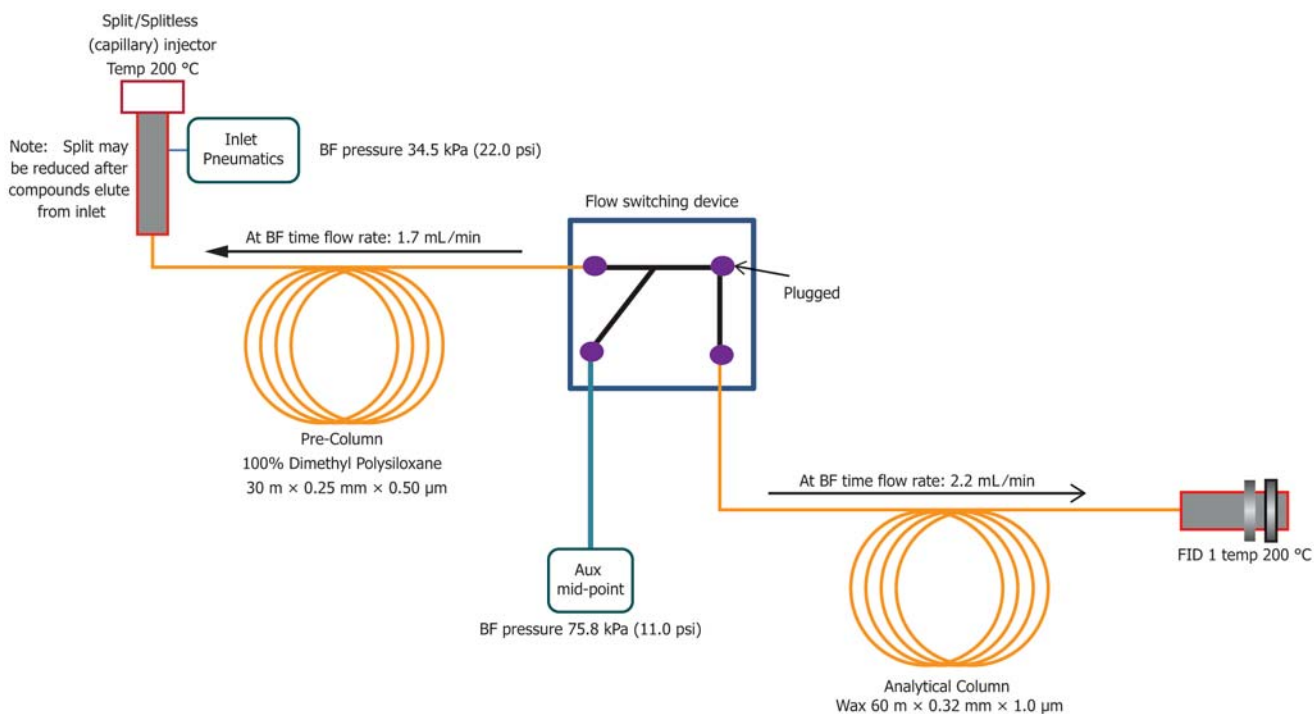


FIG. A1.6 Configuration C—Demonstrates How Backflushing is Accomplished After Elution of Toluene

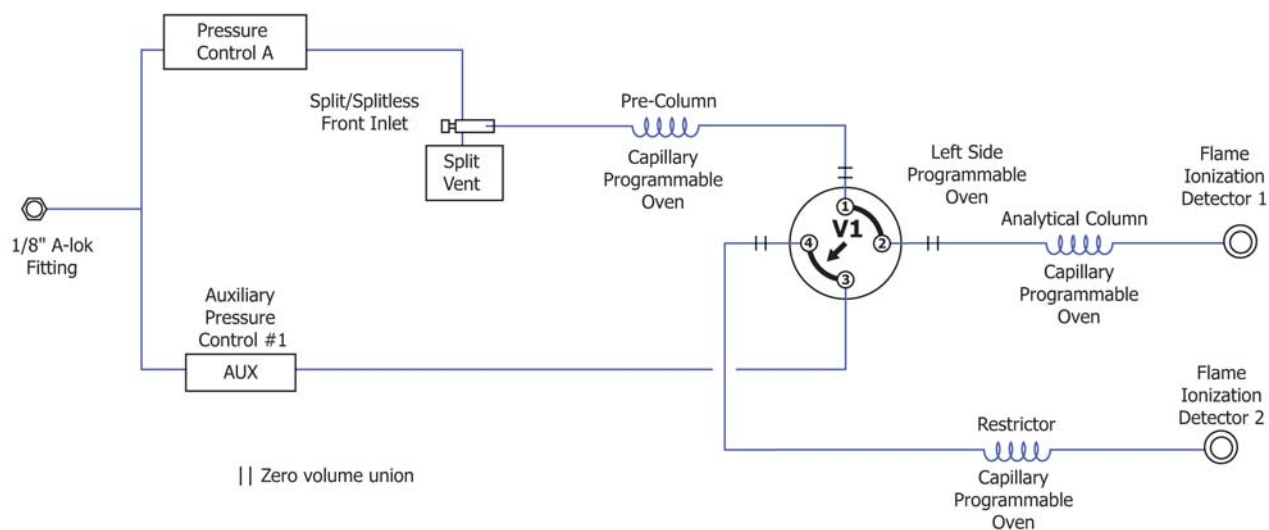


FIG. A1.7 Example of Valve Configuration

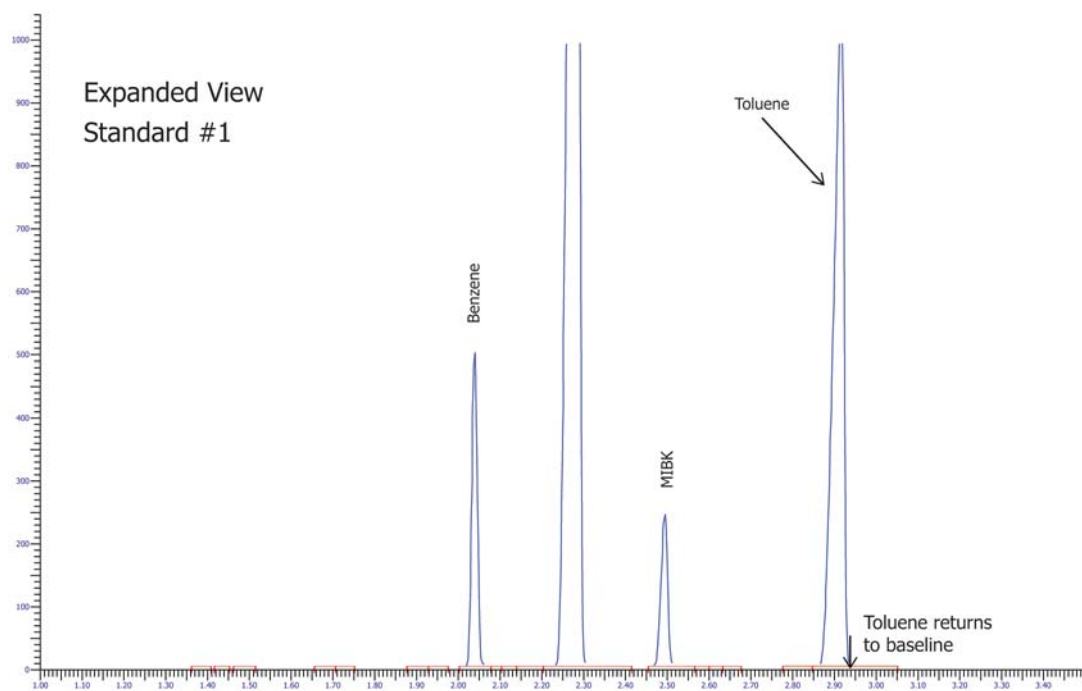


FIG. A1.8 Example of Configuration A Chromatography of Standard #1 Described in 8.2 from Pre-column

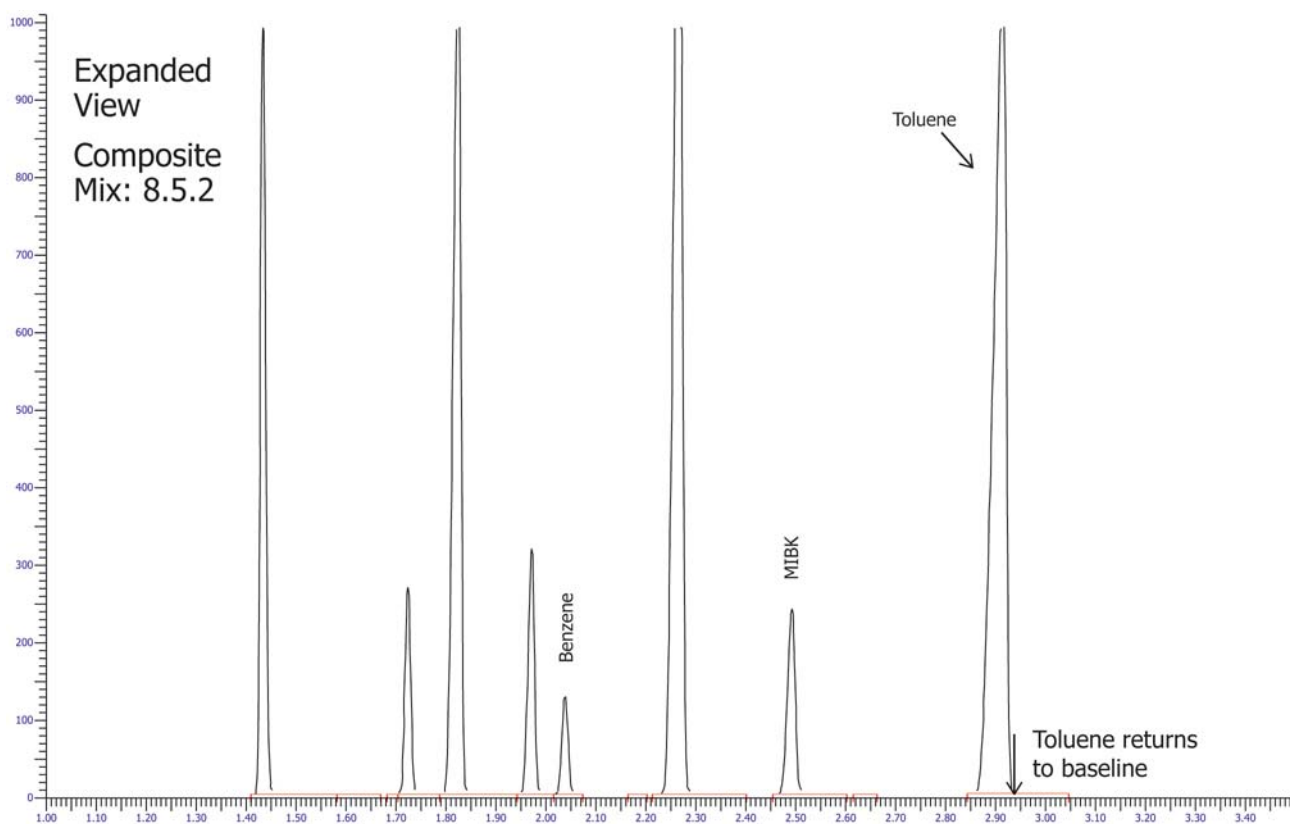


FIG. A1.9 Example of Configuration A Chromatography Through Pre-column for Composite Mix Described in 8.5.2

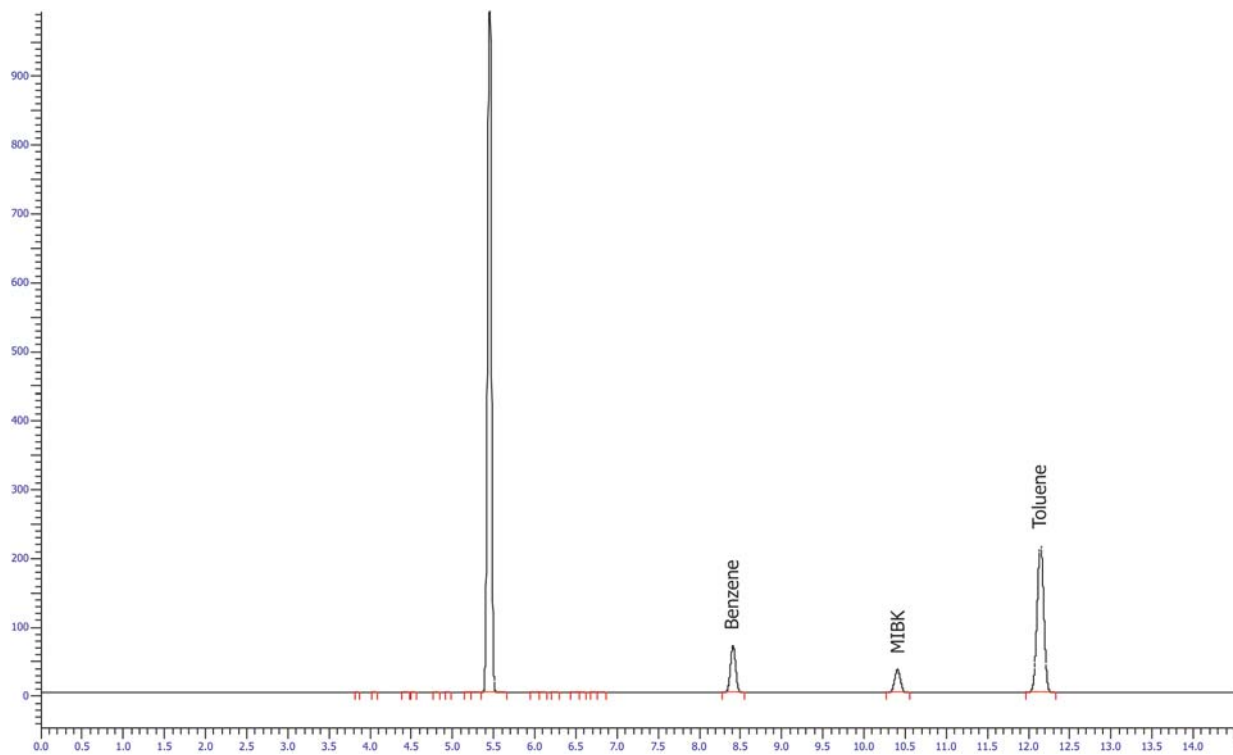
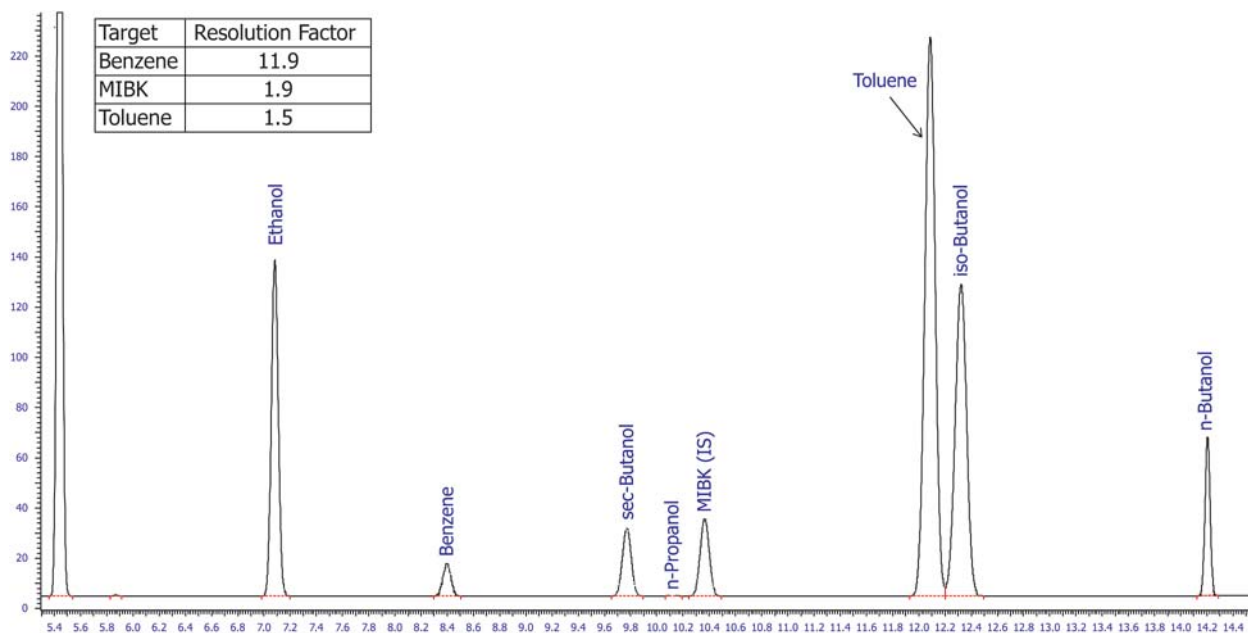


FIG. A1.10 Example Configuration A Chromatogram of Standard #1 Described in 8.2 Elution from Column B (Analytical Column)



NOTE 1—*sec*-Butanol, *n*-Propanol, *iso*-Butanol and *n*-Butanol should only be present in butanol blended fuel.

FIG. A1.11 Example Configuration A Chromatogram of Composite Mix Described in 8.5.2 Through Column B (Analytical Column)

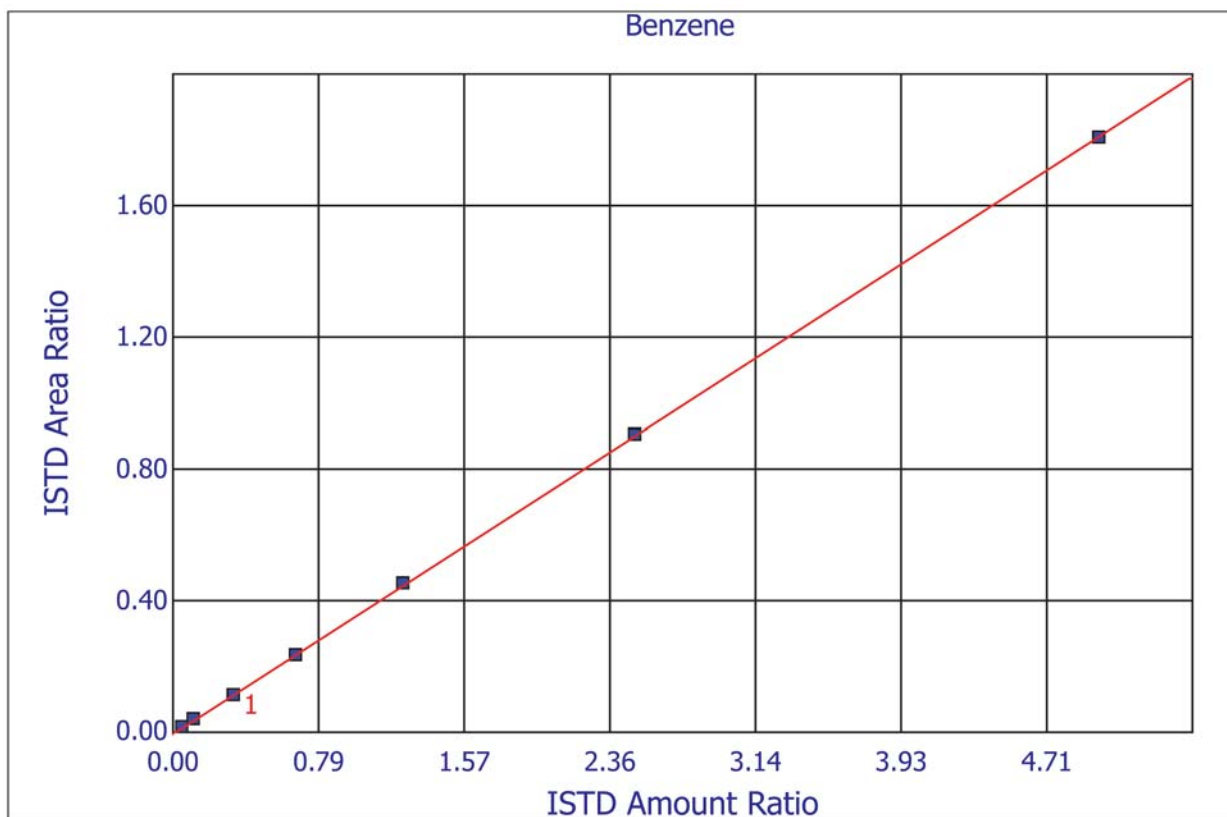


FIG. A1.12 Example Calibration Curve for Benzene Correlation Coefficient $r^2 = 0.9999$

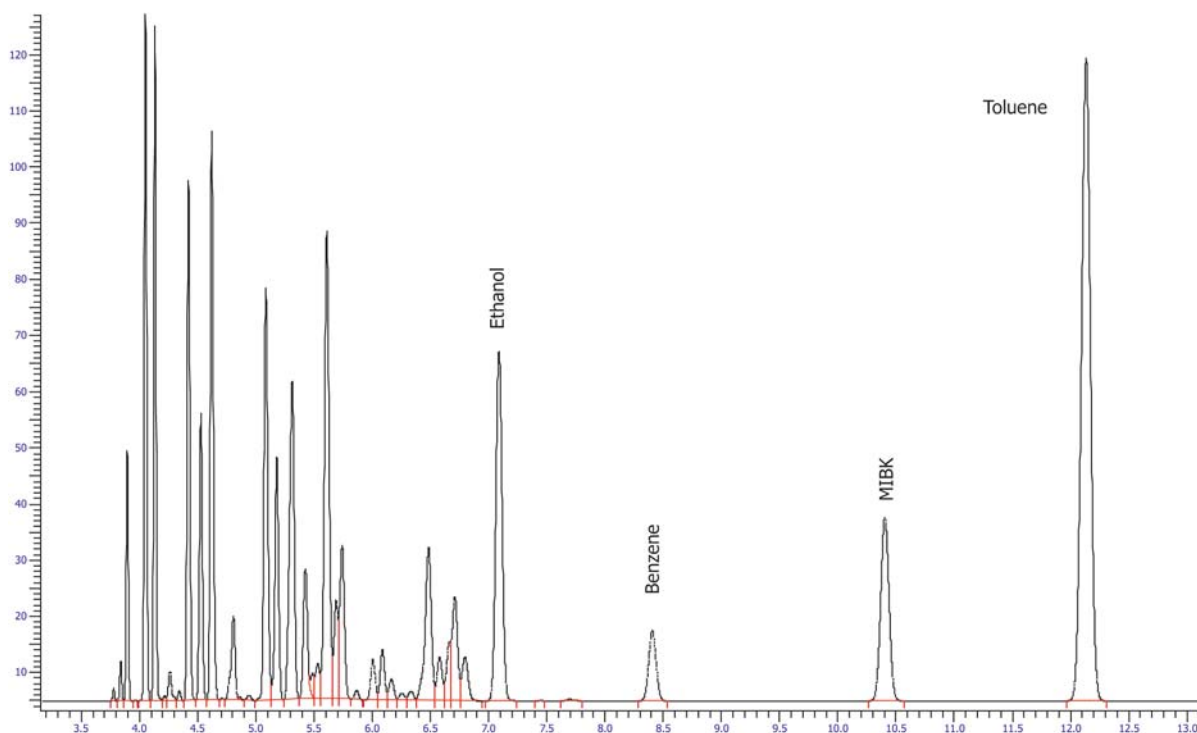
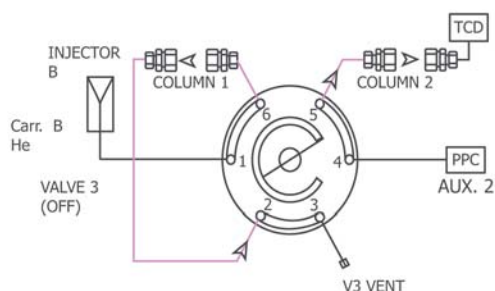


FIG. A1.13 Configuration A Chromatogram of ASTM Cross Check Sample RFG1312, Ethanol Blend

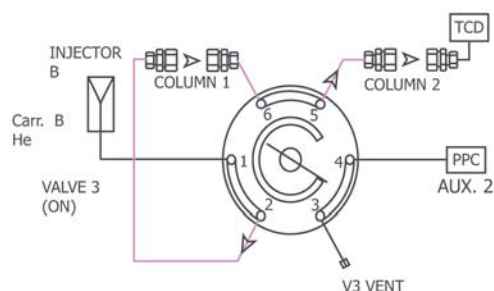
A2. PROCEDURE B (PACKED COLUMN SYSTEM)

A2.1 These configurations and operating conditions are approximate and may require optimization for each instrument and configuration. Unlike Procedure A, the removal of interference from presence of ethanol, and butanols used in fuel blending in the analysis of benzene has been a critical issue in using the packed columns in Procedure B. As a result, several approaches for the use of packed column that have been used successfully are described in this Annex. Note that some of these approaches use either sec-butanol or MEK as the internal standard to function properly. It is possible that configurations

of pressure switching and/or valve switching may vary among manufacturers. It is important that all critical parameters such as resolution, calibration linearity, quality control, and so forth be met as specified in this test method to ensure accurate results. Consult manufacturer for guidance on the use of turnkey instrumentation which is available from several vendors.



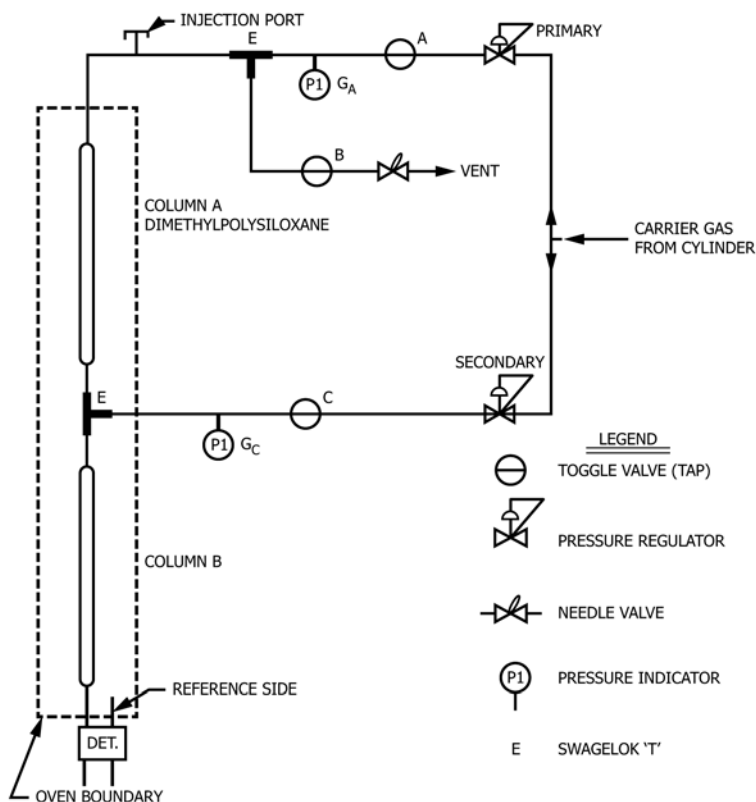
Column 1 shown in backflush mode



Column 1 and 2 shown in series during sample injection

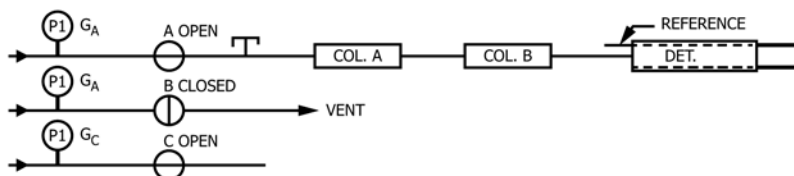
FIG. A2.1 Procedure B (Packed Column) Example Configuration With Valve Backflush

A. PIPING AND INSTRUMENTATION



B. FLOW SWITCHING SYSTEM

1. FORWARD FLOW



2. BACKFLUSH

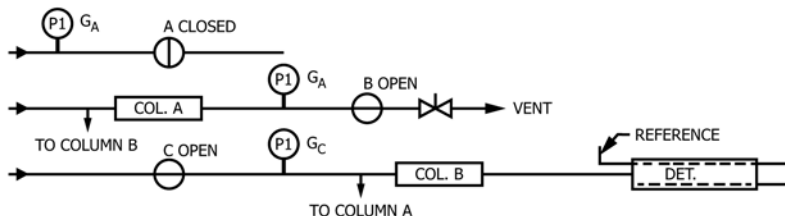


FIG. A2.2 Procedure B (Packed Column) Example Configuration with Pressure Backflush

A2.2 Packed Column Approach 1 for Procedure B: Resolving Benzene From Ethanol Using Packed Column System:

A2.2.1 A packed column set used in this test method is described below; it was developed⁶ to more accurately quantify

benzene in gasoline containing the oxygenate ethanol. A requirement for such column or equivalent is that a resolution (R_S) values for ethanol/benzene pair and *sec*-butanol/benzene pair of >1.5 be obtained when used in the configuration of B to eliminate ethanol interference with benzene and the internal standard *sec*-butanol interference with benzene. The analytical packed column contains a proprietary chromatographic phase. The two column set can be used to quantify benzene in gasoline with or without ethanol. The robustness of the column set also permits the use of N_2 (nitrogen) carrier gas with no

⁶ The sole source of supply of Column 2 known to the committee at this time is Restek, Inc., 110 Benner Circle, Bellefonte, PA 16823. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

detrimental analytical effects (see Fig. A2.5); however, the precision indicated in the test method was developed using helium only.

A2.2.2 A two column set is employed in the following order (see Fig. A2.4):

A2.2.2.1 *Column 1*—6 ft (1.8 m) × ⅛ in. OD × 2 mm ID (10 % Rtx 1 on 100/120 Silcoport)—Nonpolar Backflush.

A2.2.2.2 Backflush valve.

A2.2.2.3 *Column 2*—15.5 ft (4.76 m) × ⅛ in. × 2 mm ID (BenzoSep proprietary polymer)—Analytical Column.⁶

A2.2.2.4 TCD—Detector.

NOTE A2.1—It is acceptable to replace the MXT (Restek) Column 1 (which is the nonpolar PDMS backflush column) with a column from an alternative supplier. However, it is imperative that the tubing and the solid support used to prepare the PDMS packing material be properly deactivated to prevent excessive tailing of the ethanol into benzene. Should this occur, accurate quantitation of benzene will be difficult, if not impossible. The symmetry value (S) of ethanol at 10 % peak height should not exceed 2.8 when using an alternative Column 1. The symmetry value of ethanol can be calculated either electronically or manually as follows (see Fig. A2.5) by drawing a vertical line from the apex of the ethanol peak down to the baseline, dividing the peak into two sections. The peak height of ethanol is then measured from the apex to the baseline. This value is multiplied by 10 % and the resulting value is measured and marked above the baseline inside the peak. A horizontal line is then drawn parallel to the baseline through the 10 % peak height indicating mark. As indicated in Fig. A2.5, the leading edge of the peak is designated as “A” and the trailing edge of the peak is designated as “B.” The distance is measured from the peak leading edge and trailing edge to the vertical line at 10 % peak height. The symmetry value is then determined as $S = B/A$.

A2.2.2.5 The total length of the two set of columns is 21 ft (6.57 m). The nonpolar backflush column and the main analytical column are installed as illustrated in Fig. A2.4. A chromatogram from such system is shown in Fig. A2.5.

A2.2.3 *Examples of Operating Conditions Information:*

A2.2.3.1 Table A2.1 gives examples of operating conditions using the column set described in A2.2 and configuration in Fig. A2.2 (valve system) for Procedure B. Note that backflush time needs to be established with each column set and individual system. Flow rates and oven temperature may need to be modified to attain the required resolution for benzene. Consult manufacturer of analyzer as necessary.

Packed Column Approach 2 for Procedure B—The following section details modification to A2.2 using another alternative packed column set developed⁶ to more accurately quantify benzene in gasoline containing the oxygenate ethanol and butanol blends. Butanols have been considered as possible blending components for gasolines. For the analyses of benzene and toluene in the presence of ethanol GC operating conditions are similar as described for the column set in A2.2. A requirement for such column or equivalent is that a resolution (R) values >1.50 be obtained when used in the configuration of Fig. A2.4 to eliminate ethanol interference with benzene.

A2.3.1 The two analytical packed columns⁶ each contain a deposition of proprietary polymers coated on Restek’s DiatoSorb W AW solid support. The two column set can be used to quantify benzene in gasoline with or without ethanol and also with butanol blends under the following conditions:

A2.3.1.1 The two column set is configured in the following order (see Fig. A2.4 *Column 1*—7 ft (2.14 m) × ⅛ in. OD × 2 mm ID (proprietary polymer coated on DiatoSorb W AW) backflush column.

A2.3.1.2 Backflush valve.

A2.3.1.3 *Column 2*—15.5 ft (4.72 m) × ⅛ in. × 2 mm id (proprietary polymer)—Analytical Column.⁶

A2.3.1.4 FID—Detector.

NOTE A2.2—The symmetry value of ethanol must be <2.8 and can be calculated either electronically or manually as follows (see Fig. A2.3) by drawing a vertical line from the apex of the ethanol peak down to the baseline, dividing the peak into two sections. The peak height of ethanol is then measured from the apex to the baseline. This value is multiplied by 10 % and the resulting value is measured and marked above the baseline inside the peak. A horizontal line is then drawn parallel to the baseline through the 10 % peak height indicating mark. As indicated in the drawing below, the leading edge of the peak is designated as “A” and the trailing edge of the peak is designated as “B.” The distance is measured from the peak leading edge and trailing edge to the vertical line at 10 % peak height. The symmetry value is then determined as $S = B/A$.

A2.3.1.5 The total length of the two column set is 22.5 ft (6.86 m). Column 1, the backflush column and the main analytical column 2 are installed as illustrated in Fig. A2.4.

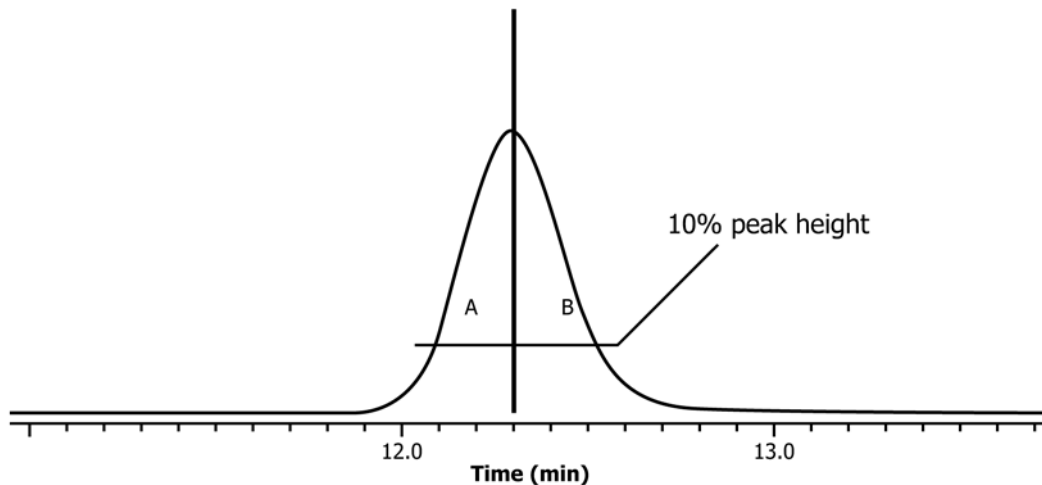


FIG. A2.3 Symmetry Value of Ethanol

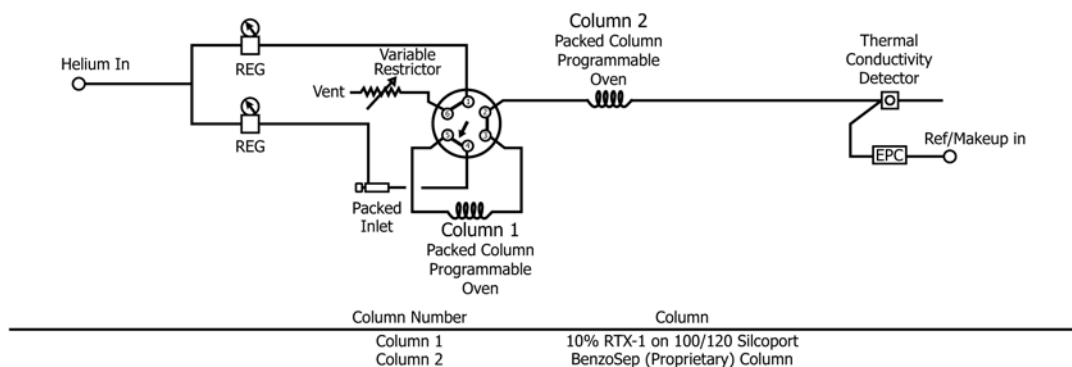


FIG. A2.4 Two Column Set

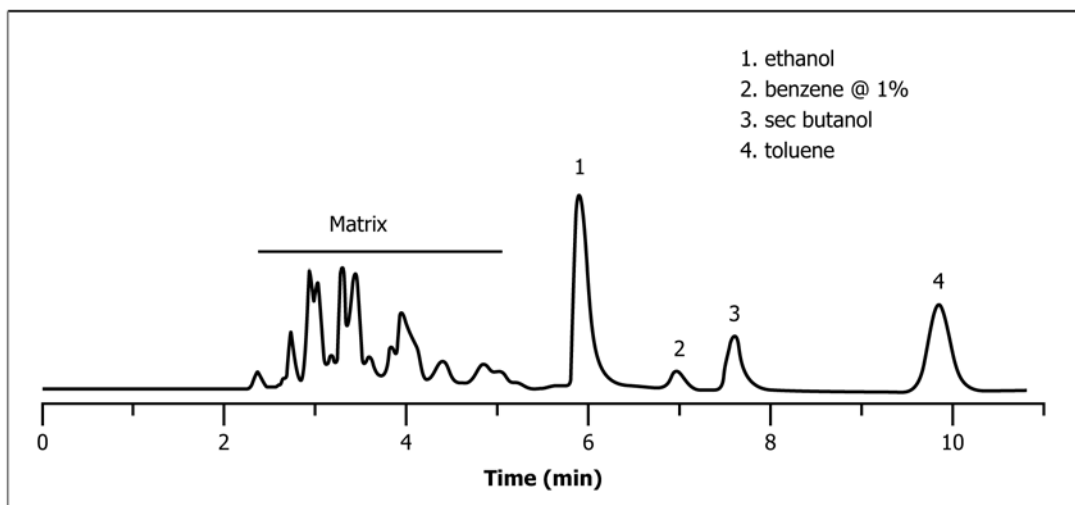


FIG. A2.5 Chromatogram of Spark Ignition Fuel ('Gasoline') Using Configuration in Fig. A2.4

TABLE A2.1 Examples of Operating Conditions for Procedure B

NOTE 1—Backflush time must be determined for each column system.

Parameter	Procedure B (Example 1)	Procedure B (Example 2)	Procedure B (Example 3)
A: Pre-column	6 ft (1.8 m), 1/8 in. OD, 2.0 mm ID, nonpolar	6 ft (1.8 m), 1/8 in. OD, 2.0 mm ID, nonpolar	6 ft (1.8 m), 1/8 in. OD, 2.0 mm ID, nonpolar
B: Analytical Column	16 ft (4.9 m), 1/8 in. OD, 2.0 mm ID, proprietary packing material	16 ft (4.9 m), 1/8 in. OD, 2.0 mm ID, proprietary packing material	16 ft (4.9 m), 1/8 in. OD, 2.0 mm ID, proprietary packing material
Flow rate (analytical column)	25.0 mL/min	30.0 mL/min	44.0 mL/min
Aux Flow	25.0 mL/min	30.0 mL/min	44.0 mL/min
Oven Parameters	135 °C hold 12 min	125 °C hold 13 min	135 °C hold 20 min
Injector Temp	200 °C	200 °C	200 °C
Detector Temp (TCD)	200 °C	200 °C	200 °C
Valve	Time 0: ON Time 3 min: OFF	Time 0: ON Time 2 min: OFF	Time 3 min: OFF Time 19.95 min: ON
Backflush time	3.0 min	2.0 min	3.0 min
Injection Volume	1.0 µL	1.0 µL	1.0 µL

A2.3.1.6 For analysis of fuels containing ethanol and butanols:

(1) The internal standard is changed from *sec*-butanol to 2-butanone (methyl ethyl ketone or MEK) when butanols are

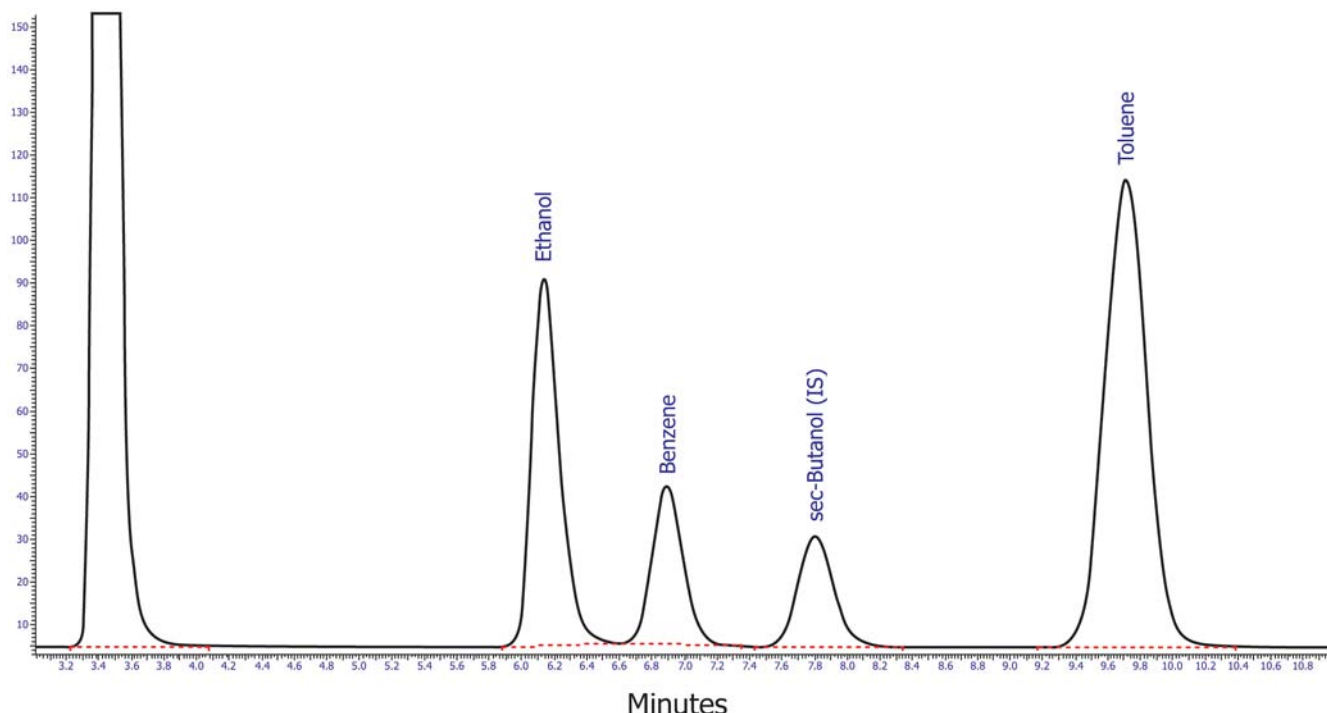


FIG. A2.6 Example Chromatogram of Calibration Standard with 2-butanol (*sec*-butanol) as the Internal Standard using Configuration in Fig. A2.2 and Column Set Described in A2.2

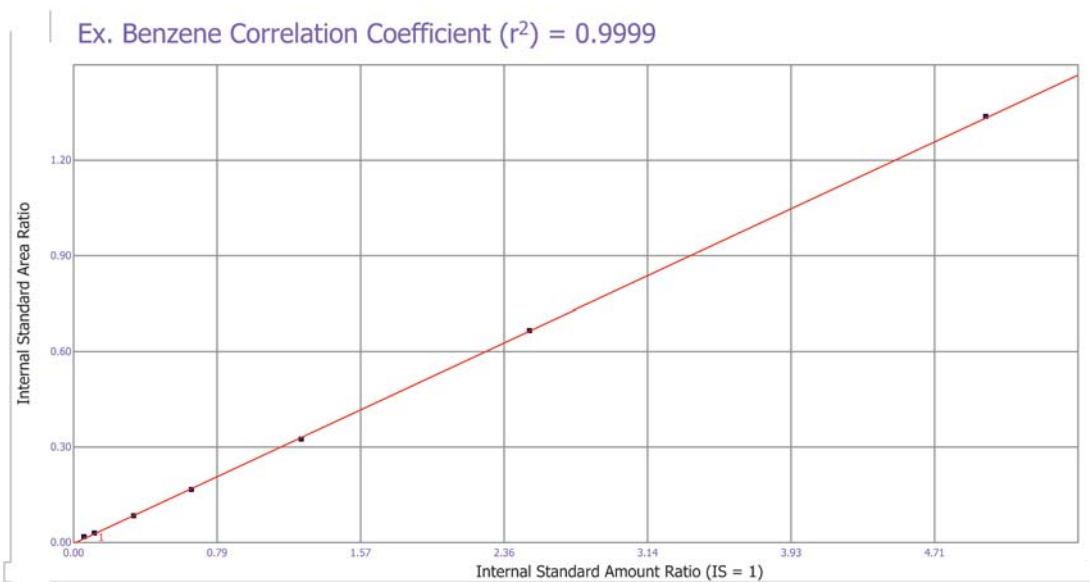


FIG. A2.7 Example Calibration Curve for Benzene Using Configuration in Fig. A2.2 and Column Set Described in A2.2

present. MEK is acceptable as an internal standard as it was used to develop precision of D3606 (RR:D02-1042⁴).

(2) For ethanol only blended fuels, the gas chromatographic parameter changes are as follows: Column Temperature Isothermal at 135 °C Column; Head Pressure approximately 393 kPa to 421 kPa; Flow Rate approximately 25 cm³/min.

(3) For butanol blended fuels, gas chromatographic parameters are as follows: 75 °C (3 min) > 5 °C/min > 85 °C (6 min)

> 20 °C/min > 135 °C (10 min). Column head pressure 343 kPa to 421 kPa at 135 °C; Flow rate 25 mL/min of He.

(4) A same chromatogram with helium carrier using this modification is given in Fig. A2.8.

(5) The column set also is appropriate for N₂ (nitrogen) carrier gas with no detrimental resolution effects (see Fig. A2.9). However, nitrogen has not been used to develop the precision of Procedure B (or Procedure A) of this test method.

Oven temperature 135 C

Flow rate 25 ml/min

Sample: Gasoline containing ethanol

Sample size: 1.5 ul

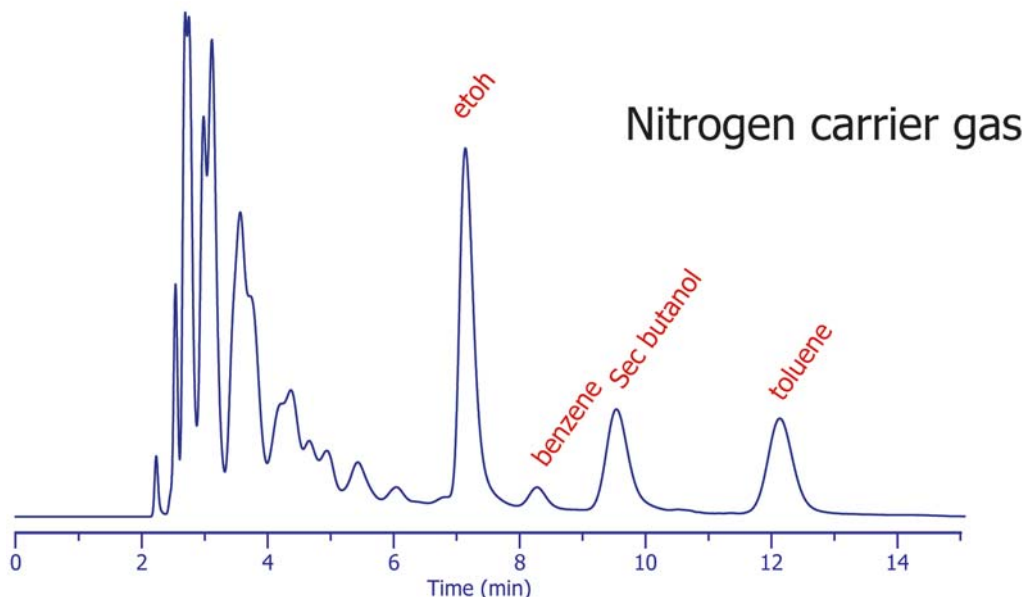


FIG. A2.8 Chromatogram of Packed Column Approach 2 of Procedure B using the Alternative Two Column Set with Helium as the Carrier Gas

NOTE A2.3—At this time, because the test method precision and bias performance information using nitrogen as a carrier gas has not been studied in accordance with the proper ASTM ILS process, the example with nitrogen carrier gas is included only for information purposes. Results obtained under the conditions using nitrogen as the carrier gas in this annex are not considered to be valid D3606 Procedure B results, and shall not be represented as such.

(6) A sample chromatogram for the analysis of benzene and toluene in the presence of butanols is shown in Fig. A2.10.

A2.4 Packed Column Approach 3 for Procedure B:

A2.4.1 The following second approach to packed columns selection is based on a suggested EPA Q&A document and is presented here. It may offer guidance to users of the test method as an alternative to Approach A2.2 and A2.3 where Approach A columns may not be readily available. Such column configuration has not been tested in the presence of butanols.

A2.4.2 Three column sections are employed, in the following order:

A2.4.2.1 Column 1—5 ft × 1/8 in. ID methyl silicone on Chromosorb (10 % OV101 on Chromosorb PAW 80/100).

A2.4.2.2 Column 2—5 ft × 1/8 in. ID TCEP on Chromosorb (20 % TCEP on Chromosorb PAW 80/100).

A2.4.2.3 Column 3—15 ft × 1/8 in. ID Carbowax 1540 (15 %) on Chromosorb W 60/80.

A2.4.2.4 This combined 20 ft section of columns 2 and 3 is connected such that the TCEP end of the combined column is toward the valve (which places the Carbowax end next to the detector). See Fig. A2.11 for a valve diagram showing the arrangement of the columns.

A2.4.2.5 The internal standard is 2-butanol (sec-butyl alcohol or SBA).

A2.4.2.6 Gas chromatographic parameters are approximately as follows:

Column Temperature	Isothermal at 135 °C
Column Head Pressure	Approximately 65 psi
Volume Flow Rate	Approximately 26.6 cm ³ /min

A2.4.2.7 For a sample chromatogram using this modification, see Fig. A2.12.

75 > 3 min > 5/min > 85 > 6 min > 20/min > 135 > 14 min

Flow rate 25 mls/min He

Sample: butanol blend gasoline spiked with butanol impurities & MEK (IS)

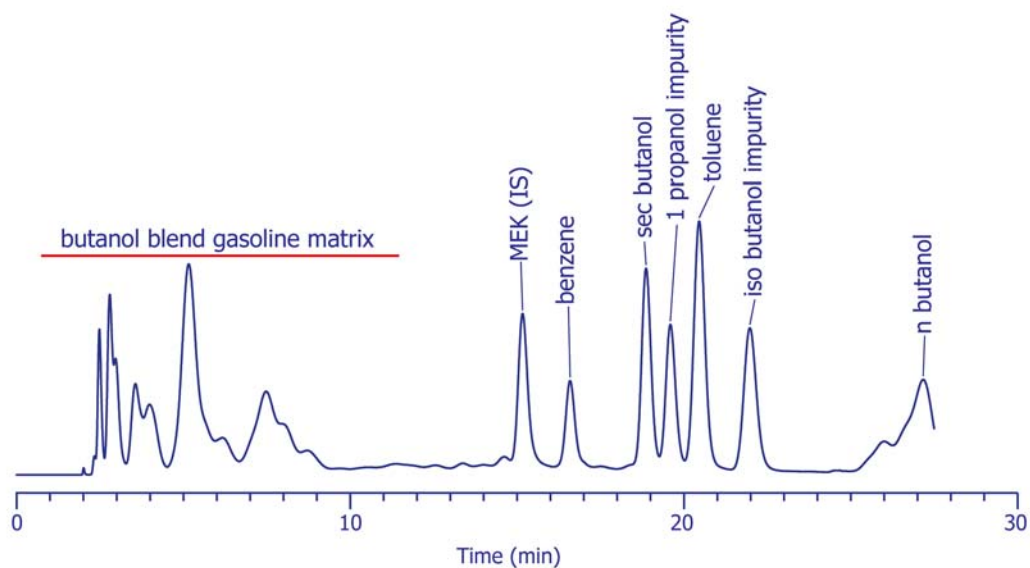


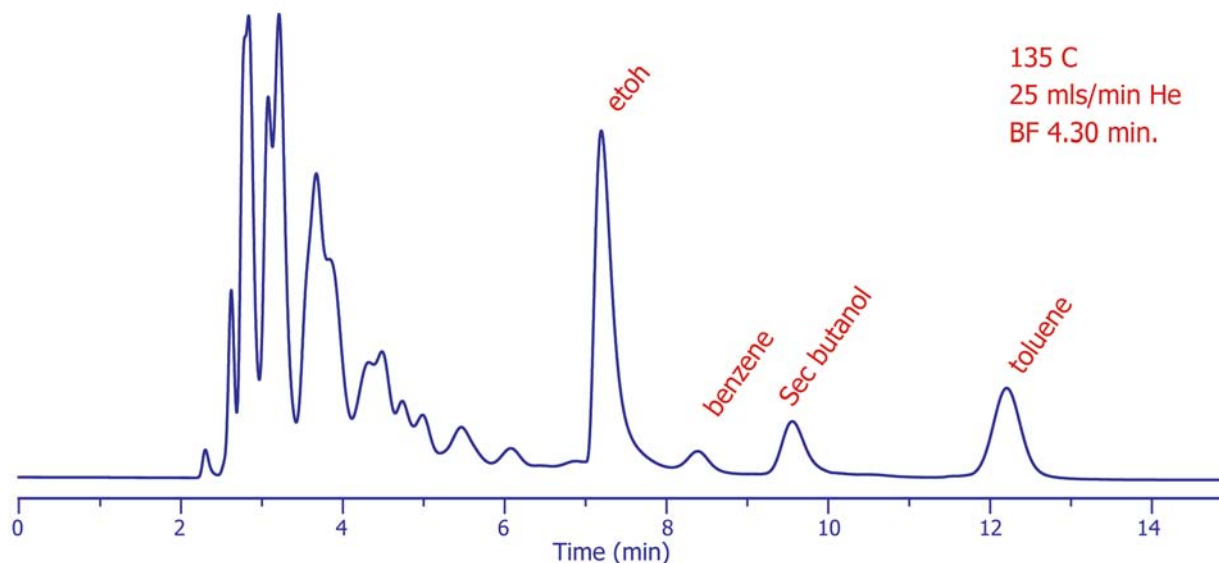
FIG. A2.9 Chromatogram of Packed Column Approach 2 of Procedure B using the Alternative Two Column Set with Nitrogen as the Carrier Gas

Oven temperature 135 C

Flow rate 25 ml/min He

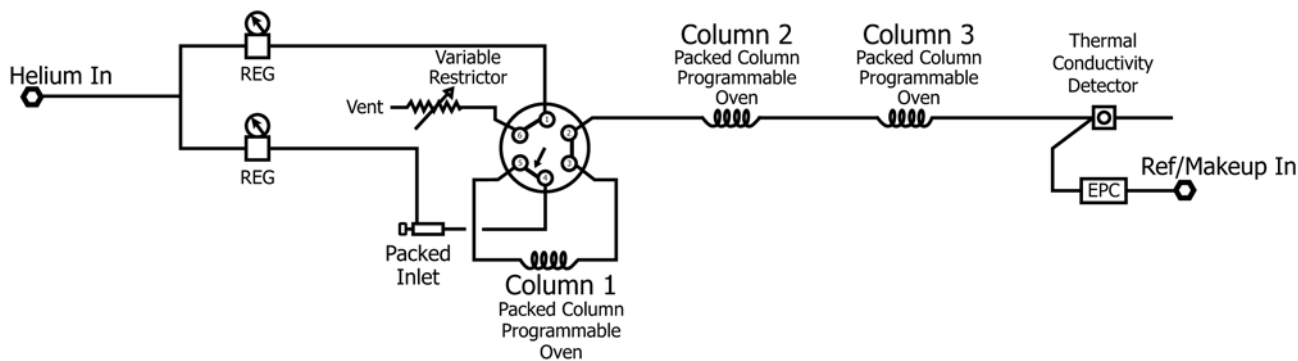
Sample: Gasoline containing ethanol

Sample size: 1.5 ul



NOTE 1—Ethanol not shown but elutes before MEK.

FIG. A2.10 Chromatogram of Packed Column Approach 2 of Procedure B using the Alternative Two Column Set with Helium as the Carrier Gas for Analyses of Benzene and Toluene in Presence of Butanols



Column Number	Column
Column 1	OV-101 Column
Column 2	TCEP Column
Column 3	CarboWax Column

FIG. A2.11 Valve Diagram Showing Arrangement of Columns for Approach 3 of Procedure B

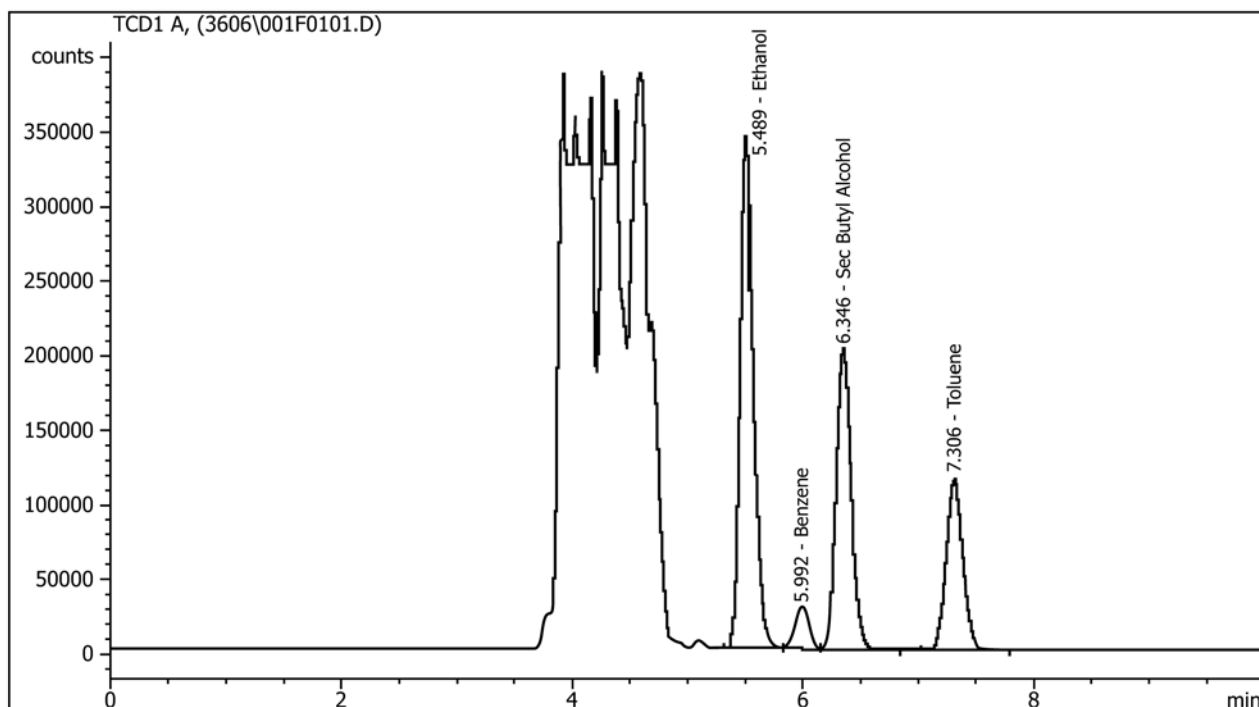


FIG. A2.12 Example Chromatogram for Improved Resolution of Benzene and Ethanol in Accordance With Fig. A2.11 GC Column Set Configuration

SUMMARY OF CHANGES

Subcommittee D02.04 has identified the location of selected changes to this standard since the last issue (D3606 – 17) that may impact the use of this standard. (Approved July 1, 2020.)

- (1) Updated Scope to clarify applicability of the method.
- (2) Added Procedure A (capillary WCOT columns) to Procedure B (packed columns) relative bias correlations for benzene and toluene.
- (3) Added Procedure B to Test Method D5769 relative bias correlation for benzene.
- (4) Added an additional gas chromatographic column set to the annex of Procedure B (packed column).
- (5) Clarified valid test method value reporting ranges and applicability of the repeatability and reproducibility functions.

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